Supporting Information for:

Convergent Synthesis of Thiodiazole Dioxides from Simple Ketones and Amines Through an Unusual Nitrogen-Migration Mechanism

Kunlayanee Punjajom [†a], Paul P. Sinclair[†a], Ishika Saha[b], Mark Seierstad[b], Michael K. Ameriks[b], Pablo García-Reynaga[b]*, Terry P. Lebold[c]*, Richmond Sarpong[a]*

[a] Department of Chemistry, University of California, Berkeley, CA 94720, USA. E-mail: rsarpong@berkeley.edu

[b] Janssen Research and Development, San Diego, California 92121, United States; Email: PGarciaR@its.jnj.com

[c] Janssen Research and Development, San Diego, California 92121, United States; Email terry.lebold@gmail.com

[†]These authors contributed equally to the project

Table of Contents

1. General Information

Unless otherwise noted, all reactions were set up in flame-dried glassware fitted with rubber septa under a positive pressure of nitrogen in anhydrous solvents using standard Schlenk techniques. Low temperature reactions were carried out in a Dewar vessel filled with a cooling agent: H_2O/ice (0° C). Reaction temperatures above room temperature (22–23 °C) were heated using silicone oil or in a heated metal block and monitored by an IKA® bar thermometer. Crude reaction mixtures were concentrated under reduced pressure on a rotary evaporator equipped with a dry ice/isopropanol condenser. Flash-column chromatography was performed using SiliaFlash P60 silica gel (Silicycle silica gel, 40-63 μm particle size). Visualization of the developed thin-layer chromatography (TLC) plate on SiliCycle Siliaplates (glass backed, extra hard layer, 60 Å, 250 μm thickness, F_{254} indicator) under UV-light (254 nm) irradiation, and subsequent heated with *p*-anisaldehyde (ANS). NMR yields were acquired using dimethyl sulfone (^{1}H NMR, $CDCl_3$) δ 3.00 (s, 6H) as the internal standard. Unless otherwise noted, yields refer to chromatographically and spectroscopically (^{1}H and ^{13}C NMR) pure material.

1.1 Materials

Commercial grade chemicals were used without further purification, unless otherwise specified. All solvents were purchased from Fisher Scientific, Alfa Aesar and Sigma Aldrich. Diethyl ether (Et_2O), tetrahydrofuran (THF), dichloromethane (DCM), and acetonitrile (MeCN) were sparged with argon and dried by passing through alumina columns using argon in a Glass Contour solvent purification system prior to use. Cyclohexane (CyH) and ethanol (EtOH) were purchased from Sigma Aldrich in SureSeal® bottles and used as received. Isotopically labeled substrates were purchased from Sigma Aldrich and used without further purification.

1.2 NMR spectroscopy

^{1}H NMR data were recorded on Bruker AV-500, NEO-500, AV-600 or AV-700 instruments operating at 500 MHz, 500 MHz, 600 MHz, or 700 MHz respecitively. ^{13}C NMR data were recorded on AV-600 or NEO-500 instruments operating at 151MHz or 126 MHz respectively. ^{19}F NMR data were recorded on JEOL-400 or Bruker AV-600 spectrometers operating at 367 MHz, or 565 MHz respectively. ^{15}N NMR data were recorded on a Bruker AV-600 operating at 61 MHz . Chemical shifts are reported in parts per million (ppm, δ), relative to the residual solvent signal of chloroform δ 7.26 (^{1} H NMR), δ 77.16 (^{13}C{^{1}H} NMR), or relative to hexafluorobenzene at δ -164.9 (^{19}F{^{1}H} NMR). Coupling constants (J) are reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and app (apparent multiplicity).

1.3 Mass spectrometry

High-resolution mass spectra (HRMS) were obtained from the QB3/Chemistry Mass Spectrometry Facility at the University of California, Berkeley, on a Finnigan/Thermo LTQ-FT instrument (ESI

and EI) and at Janssen Research and Development on Agilent Technologies 6200 series ESI-TOF or Agilent 5975C GC/MSD (EI).

Note: We thank Drs. Zongrui Zhou from UC Berkeley and Dr. Mona Sharar, Deszra Shariff, and Heather Mcallister from Janssen Research and Development for mass spectrometry acquisition and analysis.

1.4 X-ray analysis

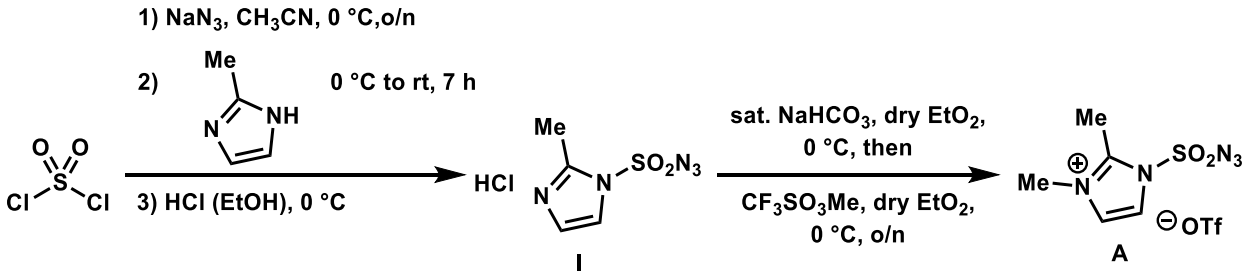
Single-crystal X-ray diffraction experiments were carried out at the UC Berkeley CHEXRAY crystallographic facility. All compounds were measured using a rotation anode Rigaku XtaLAB P200 equipped with a Pilatus 200K hybrid pixel array detector. Data were collected using either Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.5406 Å). CYLview was used for graphic rendering.

Note: We thank Dr. Nicholas Settineri at University of California Berkeley *for assistance with X-ray acquisition and crystallographic analysis.*

1.5 Melting point

Melting points for solid compounds were obtained using a MELTEMP® melting point apparatus.

2. Synthesis of 1-(azidosulfonyl)-2,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate



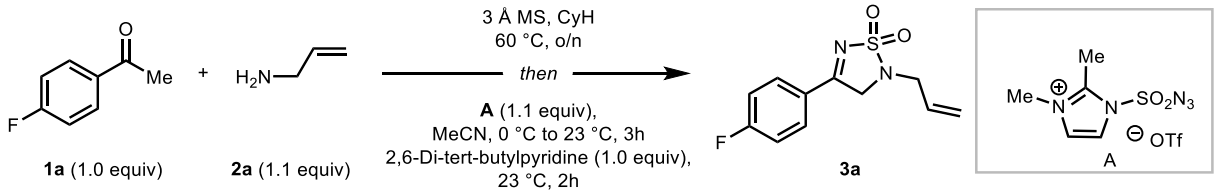
To a flame dried 100 ml round-bottomed flask was added NaN_3 (1.45 g, 0.022 mmol, 1.0 equiv) and the flask was evacuated/ backfilled with N_2 three times. Dry MeCN (22.5 mL) was added and the solution was cooled to 0 °C. To the vigorously stirring cloudy suspension was added SO_2Cl_2 (1.79 mL, 0.022 mmol, 1.0 equiv) dropwise at 0 °C. The ice bath was allowed to melt and stirring was continued overnight at room temperature. The reaction mixture was then cooled to 0 °C and then 2-methylimidazole (3.65 g, 0.044 mmol, 2.0 equiv) was added portion-wise over 15 mins. Stirring was continued for 15 mins at 0 °C, then the cold bath was allowed to warm to room temperature slowly over 7 h. H_2O (25 mL) was slowly added and the resulting mixture was stirred for 15 mins and then extracted with dry Et_2O (3 x 20 mL), washed $NaHCO_3$ (30 mL), brine, then dried over $MgSO_4$. The mixture was filtered to remove the drying agent using dry Et_2O (50 mL) to rinse the filter cake. A magnetic stir bar was added to the collection flask and the filtrate was then cooled to 0 °C with rapid stirring. To this mixture was added anhydrous HCl (prepared by slowly adding acetyl chloride (2.37 mL, 0.33 mmol, 1.5 equiv) to stirring absolute EtOH (7.8 mL) at room temperature in a flame-dried round-bottomed flask) generate a white crystalline precipitate. The precipitate was filtered using a Buchner funnel and washed with dry Et_2O (50 mL) to obtain **I** as a white solid.

The sulfuryl imidazole hydrochloride (**I**) (2.0 g, 8.9 mmol, 1.0 equiv) was dissolved in dry Et_2O (5 mL) and sat. $NaHCO_3$ (20 mL) was added until the evolution of gas was no longer observed. The mixture was extracted with dry Et_2O (3 X 50 mL), dried over anhydrous $MgSO_4$, and filtered to obtain the free base of the sulfuryl imidazolium salt in dry Et_2O. The solution was placed under an N_2 atmosphere and cooled to 0 °C. Methyl triflate (1.0 mL, 9.4 mmol, 1.05 equiv) was added drop-wise, leading to the formation of a white precipitate. The reaction was gently stirred at 0 °C overnight (using an EYELA PSL reactor). The resulting white precipitate was filtered using a Buchner funnel and washed with dry Et_2O (50 mL) to give **A** (1.83 g, 5.2 mmol, 58%) as a white solid.

This approach was adapted from a procedure reported by Fokin.[1] The ^1H NMR characterization data is fully consistent with that reported in the literature.

3. Synthesis and characterization of dihydro-1,2,5-thiodiazole 1,1, dioxides

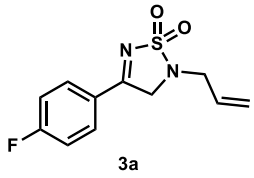
A representative procedure for the synthesis of 2-allyl-4-(4-fluorophenyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (**3a**) is provided.



To a flame-dried 20 ml vial equipped with a septum cap, *p*-fluoroacetophenone (44 µL, 0.36 mmol, 1.0 equiv) and activated 3 Å molecular sieves (100 mg) were added. The vial was evacuated and back-filled with N_2 gas three times. Cyclohexane (1.8 mL) was added followed by allyl amine (30 µL, 0.40 mmol, 1.1 equiv). The septum cap was switched for a teflon cap and reaction mixture was stirred at 60 °C for 24 h. The solvent was then removed under vacuum, and the vial was cooled to 0 °C. In a separate flame-dried 20 mL vial, imidazolium sulfonyl azide **A** (140 mg, 0.40 mmol, 1.1 equiv) was dissolved in 1.8 mL of dry MeCN and this solution was slowly added to the reaction mixture, which was allowed to warm to room temperature. After 3 h, 2,6-di-tert-butylpyridine (81 µL, 0.36 mmol, 1.0 equiv) was added at room temperature (23 °C) and stirring was continued for an additional 2 h. The reaction mixture was filtered through silica gel and celite and concentrated under reduced pressure to give the crude product which was purified by silica gel column chromatography — eluting with 20% EtOAc/hexane to obtain 2-allyl-4-(4-fluorophenyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (**3a**) (65.8 mg, 0.36 mmol, 71%) along with 18% of recovered starting material (8.8 mg, 0.36 mmol, 18%).

3a-x were all synthesized following this representative procedure. Detailed yields for these cases are listed below.

2-allyl-4-(4-fluorophenyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3a)



3a

Yield: 65.8 mg, 71% (0.36 mmol scale), yellow solid.

Melting point: 94–96 °C

New compound

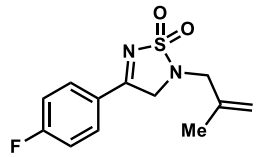
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99-7.92 (m, 2H), 7.25-7.18 (m, 2H), 5.96 (m, 1H), 5.41 (dq, J = 17.1, 1.4 Hz, 1H), 5.35 (dq, J = 10.1, 1.4 Hz, 1H), 4.56 (s, 2H), 3.90 (dt, J = 6.5, 1.3 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.5, 166.9 (d, J = 258.7 Hz), 132.0, 131.3 (d, J = 10.0 Hz), 125.7, 125.7, 120.7, 117.0 (d, J = 22.7 Hz), 56.3, 49.4.

^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -104.1 - -104.2 (m).

HRMS (ESI) *m/z* calcd for $[C_{11}H_{12}O_2N_2FS]^+$ $[M + H]^+$: 255.0598, found 255.0597.

4-(4-fluorophenyl)-2-(2-methylallyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3b)



3b

Yield: 70.7 mg, 73% (0.36 mmol scale), white solid. (9.3 mg, 19% RSM)

Melting point: 108–110 °C

New compound

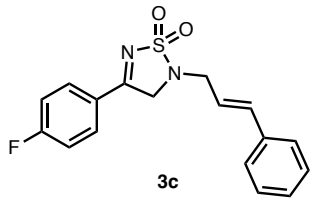
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97-7.91 (m, 2H), 7.23-7.16 (m, 2H), 5.07 (d, J = 1.6 Hz, 1H), 5.02 (d, J = 1.6 Hz, 1H), 4.52 (s, 2H), 3.76 (s, 2H), 1.82 (s, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.5, 166.8 (d, J = 258.4 Hz), 139.9, 131.3 (d, J = 9.7 Hz), 125.7 (d, J = 3.2 Hz), 116.9 (d, J = 22.2 Hz), 115.5, 56.7, 52.9, 20.0.

^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -104.2 - -104.3 (m).

HRMS (ESI) *m/z* calcd for $[C_{12}H_{14}O_2N_2FS]^+$ $[M + H]^+$: 269.0755, found 269.0757.

2-cinnamyl-4-(4-fluorophenyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3c)



3c

Yield: 7.9 mg, 33% (0.072 mmol scale), yellow solid. (0.8 mg, 8% (RSM(1a), 4.3 mg, 45% RSM(2c))

Melting point: 118–120 °C

New compound

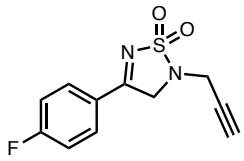
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99-7.92 (m, 2H), 7.43-7.39 (m, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.32-7.27 (m, 1H), 7.24-7.17 (m, 2H), 6.70 (d, J = 15.8 Hz, 1H), 6.32 (dt, J = 15.8, 6.8 Hz, 1H), 4.60 (s, 2H), 4.08 (dd, J = 6.8, 1.4 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.5, 166.9 (d, J = 258.7 Hz), 135.8, 135.7, 131.4 (d, J = 9.7 Hz), 128.9, 128.6, 126.8, 125.7 (d, J = 3.3 Hz), 122.8, 117.0 (d, J = 22.4 Hz), 56.1, 48.9.

^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -104.1 (s).

HRMS (ESI) *m/z* calcd for $[C_{17}H_{15}O_2N_2FNaS]^+$ $[M + Na]^+$: 353.0730, found 353.0733.

4-(4-fluorophenyl)-2-(prop-2-yn-1-yl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3d)



3d

Yield: 26.6 mg, 29% (0.36 mmol scale), yellow solid. (29.5 mg, 59% RSM)

Melting point: 150–152 °C

New compound

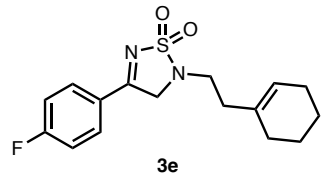
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03-7.97 (m, 2H), 7.28-7.20 (m, 2H), 4.74 (s, 2H), 4.13 (d, J = 2.5 Hz, 2H), 2.39 (t, J = 2.5 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.6, 167.0 (d, J = 258.8 Hz), 131.5 (d, J = 9.5 Hz), 125.6 (d, J = 3.3 Hz), 117.1 (d, J = 22.5 Hz), 76.2, 75.1, 56.0, 36.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -103.8 (s).

HRMS (ESI) *m/z* calcd for $[C_{11}H_9O_2N_2FNaS]^+$ $[M + Na]^+$: 275.0261, found 275.0261.

2-(2-(cyclohex-1-en-1-yl)ethyl)-4-(4-fluorophenyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3e)



3e

Yield: 55.9 mg, 48% (0.36 mmol scale), white solid. (12.9 mg, 26% RSM)

Melting point: 192–194 °C

New compound

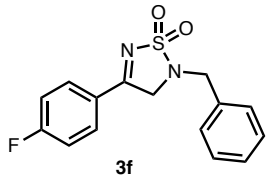
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99-7.93 (m, 2H), 7.25-7.18 (m, 2H), 5.55-5.53 (m, 1H), 4.60 (s, 2H), 3.40-3.34 (m, 2H), 2.40-2.34 (m, 2H), 2.03-1.96 (m, 4H), 1.68-1.61 (m, 2H), 1.60-1.52 (m, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.2, 166.8 (d, J = 258.3 Hz), 134.1, 131.2 (d, J = 9.5 Hz), 125.8 (d, J = 3.2 Hz), 124.1, 117.0 (d, J = 22.2 Hz), 56.9, 45.3, 37.2, 28.3, 25.4, 23.0, 22.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -104.4 (s).

HRMS (ESI) *m/z* calcd for $[C_{16}H_{20}O_2N_2FS]^+$ $[M + H]^+$: 323.1224, found 323.1224.

2-benzyl-4-(4-fluorophenyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3f)



3f

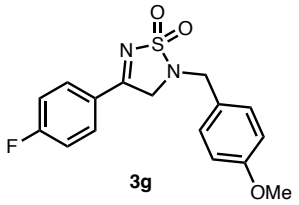
Yield: 67.5 mg, 61% (0.36 mmol scale), brown solid. (3.3 mg, 7% RSM)

Melting point: 152–154 °C

New compound

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93-7.86 (m, 2H), 7.43-7.42 (m, 2H), 7.41-7.37 (m, 2H), 7.36-7.33 (m, 1H), 7.20-7.13 (m, 2H), 4.45 (s, 2H), 4.44 (s, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.5, 166.8 (d, J = 258.4 Hz), 134.9, 131.3 (d, J = 9.5 Hz), 129.1, 128.6, 128.6, 125.6 (d, J = 3.2 Hz), 116.9 (d, J = 22.2 Hz), 56.2, 50.0.
^{19}F NMR (565 MHz, $CDCl_3$) δ -104.1 - -104.2 (m).
HRMS (ESI) *m/z* calcd for $[C_{15}H_{14}O_2N_2FS]^+$ $[M + H]^+$: 305.0755, found 305.0754.

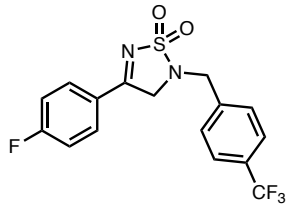
4-(4-fluorophenyl)-2-(4-methoxybenzyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3g)



3g

Yield: 42.5 mg, 35% (0.36 mmol scale), white solid. (8.1 mg, 16% RSM)
Melting point: 200–202 °C
New compound
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93-7.86 (m, 2H), 7.37-7.32 (m, 2H), 7.21-7.14 (m, 2H), 6.94-6.89 (m, 2H), 4.40 (s, 2H), 4.40 (s, 2H), 3.82 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.4, 166.8 (d, J = 258.7 Hz), 159.9, 131.3 (d, J = 9.6 Hz), 130.1, 126.8, 125.7 (d, J = 3.2 Hz), 116.9 (d, J = 22.5 Hz), 114.5, 56.0, 55.5, 49.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ -100.93 - -101.03 (m).
HRMS (ESI) *m/z* calcd for $[C_{16}H_{15}O_3N_2FNaS]^+$ $[M + Na]^+$: 357.0680, found 357.0683.

4-(4-fluorophenyl)-2-(4-(trifluoromethyl)benzyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3h)

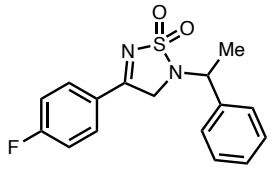


3h

Yield: 64.5 mg, 48% (0.36 mmol scale), white solid. (9.2 mg, 18% RSM)
Melting point: 165–167 °C
New compound
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96-7.89 (m, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.23-7.16 (m, 2H), 4.52 (s, 2H), 4.47 (s, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.2, 167.0 (d, J = 259.2 Hz), 139.2, 131.4 (d, J = 9.5 Hz), 131.0 (q, J = 32.5 Hz), 128.8, 126.2 (q, J = 3.8 Hz), 125.5 (d, J = 3.0 Hz), 124.0 (q, J = 272.2 Hz), 117.0 (d, J = 22.4 Hz), 56.4, 49.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ -65.9 (s), -103.6 - -103.8 (m).

HRMS (ESI) *m/z* calcd for $[C_{16}H_{12}O_2N_2F_4NaS]^+$ $[M + Na]^+$: 395.0448, found 395.0451.

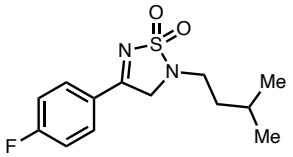
4-(4-fluorophenyl)-2-(1-phenylethyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3i)



3i

Yield: 29.7 mg, 26% (0.36 mmol scale), yellow solid. (26.6 mg, 53% RSM)
Melting point: 146–148 °C
New compound
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88-7.84 (m, 2H), 7.46-7.43 (m, 2H), 7.42-7.38 (m, 2H), 7.37-7.33 (m, 1H), 7.17-7.13 (m, 2H), 4.72 (q, J = 6.7 Hz, 1H), 4.43 (d, J = 17.4 Hz, 1H), 4.21 (d, J = 17.4 Hz, 1H), 1.81 (d, J = 6.7 Hz, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.1, 166.7 (d, J = 258.3 Hz), 140.6, 131.2 (d, J = 9.5 Hz), 129.2, 128.5, 127.2, 125.7 (d, J = 3.2 Hz), 116.8 (d, J = 22.2 Hz), 56.7, 55.0, 20.3.
^{19}F NMR (565 MHz, $CDCl_3$) δ -104.5 (s).
HRMS (ESI) *m/z* calcd for $[C_{16}H_{16}O_2N_2FS]^+$ $[M + H]^+$: 319.0911, found 319.0914.

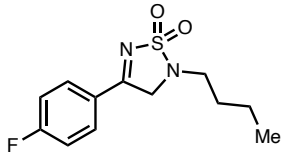
4-(4-fluorophenyl)-2-isopentyl-2,3-dihydro-1,2,5-thiadiazole 1,1-Dioxide (3j)



3j

Yield: 62.5 mg, 61% (0.36 mmol scale), white solid. (13.4 mg, 27% RSM)
Melting point: 125–127 °C
New compound
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98-7.91 (m, 2H), 7.23-7.16 (m, 2H), 4.59 (s, 2H), 3.30-3.24 (m, 1H), 1.76-1.66 (m, 1H), 1.64-1.58 (m, 2H), 0.95 (s, 3H), 0.94 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.5, 166.8 (d, J = 258.3 Hz), 131.3 (d, J = 9.5 Hz), 125.7 (d, J = 3.2 Hz), 116.9 (d, J = 22.3 Hz), 57.0, 45.2, 37.2, 25.9, 22.4.
^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -104.3 - -104.4 (m).
HRMS (ESI) *m/z* calcd for $[C_{13}H_{17}O_2N_2FNaS]^+$ $[M + Na]^+$: 307.0887, found 307.0887.

2-butyl-4-(4-fluorophenyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3k)



3k

Yield: 55.7 mg, 57% (0.36 mmol scale), white solid. (5.8 mg, 12% RSM)

Melting point: 125–127 °C

New compound

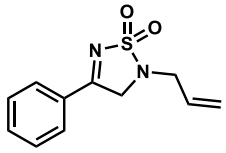
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99-7.92 (m, 2H), 7.25-7.17 (m, 2H), 4.59 (s, 2H), 3.30-3.24 (m, 2H), 1.74-1.69 (m, 2H), 1.48-1.42 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.3, 166.8 (d, J = 258.3 Hz), 131.3 (d, J = 9.8 Hz), 125.7 (d, J = 3.2 Hz), 116.9 (d, J = 22.2 Hz), 57.1, 46.6, 30.6, 20.1, 13.7.

^{19}F{^{1}H} NMR (565 MHz, $CDCl_3$) δ -104.3 - -104.4 (m).

HRMS (ESI) *m/z* calcd for $[C_{12}H_{16}O_2N_2FS]^+$ $[M + H]^+$: 271.0911, found 271.0910.

2-allyl-4-phenyl-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3l)



3l

Yield: 75.2 mg, 76% (0.42 mmol scale), white solid.

Melting point: 108–110 °C

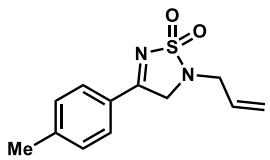
New compound

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94-7.89 (m, 2H), 7.68-7.61 (m, 1H), 7.54-7.48 (m, 2H), 6.00-5.91 (m, 1H), 5.41 (dq, J = 17.1, 1.4 Hz, 1H), 5.33 (dq, J = 10.1, 1.2 Hz, 1H), 4.59 (s, 2H), 3.90 (dt, J = 6.5, 1.3 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 174.85, 135.01, 131.99, 129.43, 129.25, 128.62, 120.60, 56.36, 49.27.

HRMS (ESI) *m/z* calcd for $[C_{11}H_{13}N_2O_2S]^+$ $[M+H]^+$: 237.0692, found 237.0696.

2-allyl-4-(p-tolyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3m)



3m

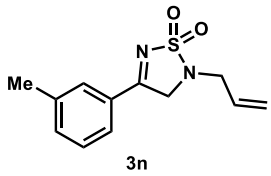
Yield: 63.2 mg, 68% (0.37 mmol scale), yellow solid. (15.2 mg, 30% RSM)

Melting point: 126–128 °C

New compound

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 6.01-5.91 (m, 1H), 5.41 (d, J = 17.1 Hz, 1H), 5.33 (d, J = 10.1 Hz, 1H), 4.56 (s, 2H), 3.89 (d, J = 6.5 Hz, 2H), 2.44 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 174.6, 146.4, 132.1, 130.2, 128.7, 126.6, 120.5, 56.3, 49.3, 22.0.
HRMS (ESI) *m/z* calcd for $[C_{12}H_{15}N_2O_2S]^+$ $[M+H]^+$: 215.0849, found 215.0853.

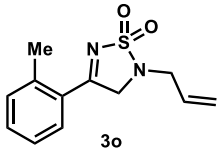
2-allyl-4-(m-tolyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3n)



3n

Yield: 67.6 mg, 72% (0.37 mmol scale), yellow solid. (11.2 mg, 22% RSM)
Melting point: 73–75 °C
New compound
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.7 Hz, 1H), 6.00-5.90 (m, 1H), 5.41 (dq, J = 17.1, 1.4 Hz, 1H), 5.33 (dq, J = 10.1, 1.2 Hz, 1H), 4.57 (s, 2H), 3.89 (dt, J = 6.5, 1.3 Hz, 2H), 2.40 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.0, 139.4, 135.8, 132.0, 129.3, 129.2, 129.1, 125.8, 120.5, 56.4, 49.3, 21.3.
HRMS (ESI) *m/z* calcd for $[C_{12}H_{15}N_2O_2S]^+$ $[M+H]^+$: 215.0849, found 215.0852.

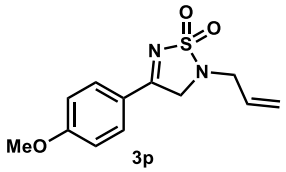
2-allyl-4-(o-tolyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3o)



3o

Yield: 7.9 mg, 9% (0.37 mmol scale), white solid. (30.2 mg, 60% RSM)
Melting point: 83–85 °C
New compound
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, J = 7.9 Hz, 1H), 7.50 (td, J = 7.6, 1.4 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.33 (td, J = 7.7, 1.3 Hz, 1H), 6.03-5.93 (m, 1H), 5.41 (dq, J = 17.1, 1.4 Hz, 1H), 5.35 (dq, J = 10.1, 1.2 Hz, 1H), 4.57 (s, 2H), 3.92 (dt, J = 6.5, 1.3 Hz, 2H), 2.72 (s, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.2, 141.9, 133.8, 133.2, 132.2, 129.6, 128.2, 126.5, 120.6, 58.2, 49.3, 23.4.
HRMS (ESI) *m/z* calcd for $[C_{12}H_{15}N_2O_2S]^+$ $[M+H]^+$: 215.0849, found 215.0842.

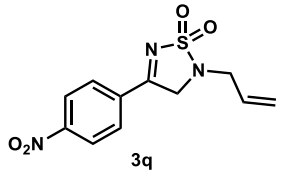
2-allyl-4-(4-methoxyphenyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3p)



3p

Yield: 22.0 mg, 25% (0.33 mmol scale), white solid. (3.5 mg, 7% RSM)
Melting point: 137–139 °C
New compound
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92-7.86 (m, 2H), 7.02-6.96 (m, 2H), 6.02-5.92 (m, 1H), 5.41 (dq, J = 17.1, 1.4 Hz, 1H), 5.33 (dq, J = 10.0, 1.2 Hz, 1H), 4.53 (s, 2H), 3.90 (s, 3H), 3.91-3.87 (m, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.7, 165.2, 132.3, 131.0, 121.8, 120.4, 114.9, 56.2, 55.9, 49.4.
HRMS (ESI) *m/z* calcd for $[C_{12}H_{14}O_3N_2NaS]^+$ $[M + Na]^+$: 289.0617, found 289.0619.

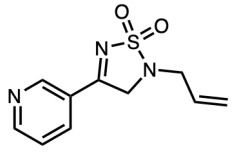
2-allyl-4-(4-nitrophenyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3q)



3q

Yield: 52.4 mg, 62% (0.30 mmol scale), yellow solid. (7.2 mg, 14% RSM)
Melting point: 186–189 °C
New compound
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40-8.36 (m, 2H), 8.15-8.11 (m, 2H), 6.02-5.92 (m, 1H), 5.44 (dq, J = 17.1, 1.5 Hz, 1H), 5.38 (dq, J = 10.1, 1.1 Hz, 1H), 4.62 (s, 2H), 3.94 (dt, J = 6.5, 1.3 Hz, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 172.8, 151.4, 134.6, 131.7, 129.7, 124.6, 121.2, 56.3, 49.3.
HRMS (ESI) *m/z* calcd for $[C_{11}H_{11}O_4N_3NaS]^+$ $[M + Na]^+$: 304.0362, found 304.0362.

2-allyl-4-(pyridin-3-yl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3r)

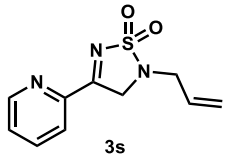


3r

Yield: 54.4 mg, 56% (0.41 mmol scale), white solid. (15.2 mg, 30% RSM)
Melting point: 117–119 °C
New compound

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.03 (d, J = 2.3 Hz, 1H), 8.84 (dd, J = 4.9, 1.7 Hz, 1H), 8.28 (dt, J = 8.2, 2.0 Hz, 1H), 7.49 (dd, J = 8.2, 4.9 Hz, 1H), 5.99-5.89 (m, 1H), 5.42 (d, J = 17.6 Hz, 1H), 5.35 (d, J = 10.1 Hz, 1H), 4.62 (s, 2H), 3.90 (d, J = 6.5 Hz, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.2, 155.2, 149.4, 135.9, 131.7, 125.5, 124.3, 121.0, 56.2, 49.2.
HRMS (ESI) *m/z* calcd for $[C_{10}H_{12}O_2N_3S]^+$ $[M + H]^+$: 238.0645, found 238.0645.

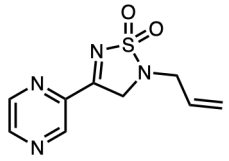
2-allyl-4-(pyridin-2-yl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3s)



3s

Yield: 86.8 mg, 89% (0.41 mmol scale), yellow solid. (3.0 mg, 6% RSM)
Melting point: 118–120 °C
New compound
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.27 (dt, J = 7.9, 1.1 Hz, 1H), 7.90 (td, J = 7.8, 1.7 Hz, 1H), 7.53 (ddd, J = 7.7, 4.8, 1.2 Hz, 1H), 5.97-5.91 (m, 1H), 5.40 (dq, J = 17.1, 1.4 Hz, 1H), 5.32 (dq, J = 10.1, 1.2 Hz, 1H), 4.72 (s, 2H), 3.90 (dt, J = 6.5, 1.3 Hz, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 176.0, 150.1, 148.1, 137.4, 131.8, 128.3, 124.1, 120.5, 56.7, 49.2.
HRMS (ESI) *m/z* calcd for $[C_{10}H_{12}O_2N_3S]^+$ $[M + H]^+$: 238.0645, found 238.0645.

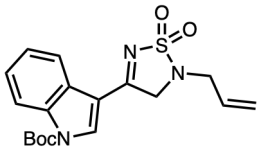
2-allyl-4-(pyrazin-2-yl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3t)



3t,

Yield: 58.6 mg, 60% (0.41 mmol scale), yellow oil.
New compound
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.45 (d, J = 1.5 Hz, 1H), 8.81 (d, J = 2.5 Hz, 1H), 8.68 (dd, J = 2.5, 1.5 Hz, 1H), 5.97-5.90 (m, 1H), 5.40 (dq, J = 17.1, 1.4 Hz, 1H), 5.33 (dq, J = 10.1, 1.4 Hz, 1H), 4.70 (s, 2H), 3.90 (dt, J = 6.5, 1.3 Hz, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 174.5, 148.8, 145.1, 144.6, 143.6, 131.6, 120.8, 56.5, 49.2.
HRMS (ESI) *m/z* calcd for $[C_9H_{11}N_4O_2S]^+$ $[M+H]^+$: 239.0597, found 239.0609.

tert-butyl 3-(5-allyl-1,1-dioxido-4,5-dihydro-1,2,5-thiadiazol-3-yl)-1H-indole-1-carboxylate (3u)



3u

Yield: 8.8 mg, 12% (0.19 mmol scale), white solid. (32.4 mg, 65% RSM)

Melting point: 134–136 °C

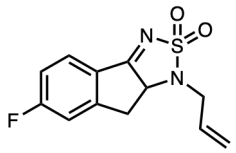
New compound

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (dd, J = 7.6, 1.5 Hz, 1H), 8.20 (s, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.46-7.39 (m, 2H), 6.04-5.95 (m, 1H), 5.43 (dq, J = 17.1, 1.4 Hz, 1H), 5.36 (dq, J = 10.1, 1.4 Hz, 1H), 4.56 (s, 2H), 3.93-3.89 (m, 2H), 1.72 (s, 9H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.3, 148.7, 135.8, 132.3, 132.3, 126.6, 126.5, 125.1, 123.0, 120.5, 115.4, 112.6, 86.6, 56.7, 49.6, 31.7, 28.2, 22.8, 14.3.

HRMS (ESI) *m/z* calcd for $[C_{18}H_{21}O_4N_3NaS]^+$ $[M + H]^+$: 398.1145, found 398.1140.

1-allyl-6-fluoro-8,8a-dihydro-1H-indeno[1,2-c][1,2,5]thiadiazole 2,2-dioxide (3v)



3v

Yield: 41.9 mg, 47% (0.33 mmol scale), white solid. (9.3 mg, 19% RSM)

Melting point: 85–87 °C

New compound

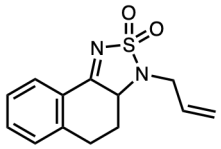
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.5, 5.1 Hz, 1H), 7.19 (dt, J = 8.7, 2.3 Hz, 1H), 7.16-7.14 (m, 1H), 5.99 (m, 1H), 5.45 (dq, J = 17.1, 1.3 Hz, 1H), 5.35 (dq, J = 10.1, 1.3 Hz, 1H), 4.41 (dd, J = 7.4, 6.0 Hz, 1H), 4.12 (ddt, J = 13.6, 5.6, 1.5 Hz, 1H), 3.66-3.59 (m, 1H), 3.43 (dd, J = 15.6, 7.4 Hz, 1H), 3.00-2.93 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 184.8, 167.8 (d, J = 259.5 Hz), 153.6 (d, J = 10.1 Hz), 132.4, 128.0 (d, J = 10.7 Hz), 125.9 (d, J = 2.4 Hz), 121.0, 117.5 (d, J = 24.0 Hz), 114.2 (d, J = 22.9 Hz), 69.8, 50.2, 37.2 (d, J = 2.2 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -102.30 (m).

HRMS (ESI) *m/z* calcd for $[C_{12}H_{12}O_2N_2FS]^+$ $[M + H]^+$: 267.0598, found 267.0598.

3-allyl-3,3a,4,5-tetrahydronaphtho[1,2-c][1,2,5]thiadiazole 2,2-dioxide (3w)



3w

Yield: 8.3 mg, 9% (0.34 mmol scale), white solid. (41.4 mg, 85% RSM) from α-tetralone

Yield: 30.0 mg, 33% (0.34 mmol scale), white solid. (20.0 mg, 40% RSM) from β-tetralone

Melting point: 148–150 °C

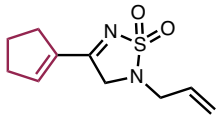
New compound

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.0, 1.4 Hz, 1H), 7.56 (td, J = 7.6, 1.4 Hz, 1H), 7.39 (t, J = 7.7 Hz, 1H), 7.30-7.28 (m, 1H), 6.09-5.99 (m, 1H), 5.43 (dq, J = 17.1, 1.4 Hz, 1H), 5.33 (dq, J = 10.1, 1.4 Hz, 1H), 4.24 (dd, J = 13.3, 5.1 Hz, 1H), 4.01-3.85 (m, 2H), 3.12-2.99 (m, 2H), 2.53-2.46 (m, 1H), 2.01-1.91 (m, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 176.7, 142.7, 135.1, 132.5, 129.3, 128.5, 127.7, 125.9, 120.5, 65.9, 48.2, 29.6, 27.4.

HRMS (ESI) m/z calcd for $[C_{13}H_{15}O_2N_2S]^+$ $[M + H]^+$: 263.0849, found 263.0848.

2-allyl-4-(cyclopent-1-en-1-yl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3x)



Yield: 47.4 mg, 46% (0.45 mmol scale), orange wax (2.4 mg, 4.8% recovered SM).

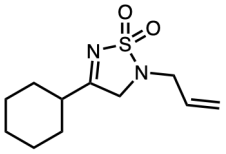
New compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (s, 1H), 5.86 (ddt, J = 16.7, 10.1, 6.5 Hz, 1H), 5.34 – 5.21 (m, 2H), 4.22 (s, 2H), 3.76 (d, J = 6.5 Hz, 2H), 2.73 – 2.52 (m, 4H), 1.97 (p, J = 7.7 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 147.9, 138.1, 132.1, 120.3, 56.2, 49.3, 34.7, 31.3, 22.7.

HRMS (ESI) *m/z* calcd for $[C_{10}H_{15}O_2N_2S]^+$ 227.0849 found: 227.0850

2-allyl-4-cyclohexyl-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3y)



3x

Yield: 67.2 mg, 70% (0.40 mmol scale), white solid.

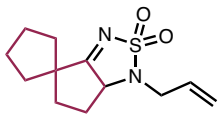
Melting point: 60–62 °C

New compound

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.92-5.82 (m, 1H), 5.33 (dd, J = 17.1, 1.4 Hz, 1H), 5.28 (dd, J = 10.1, 1.2 Hz, 1H), 4.08 (s, 2H), 3.78-3.76 (m, 2H), 2.48 (tt, J = 11.4, 3.5 Hz, 1H), 1.97-1.89 (m,

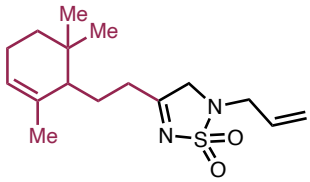
2H), 1.82 (dt, *J* = 13.1, 3.6 Hz, 2H), 1.74-1.66 (m, 1H), 1.45-1.39 (m, 2H), 1.36-1.28 (m, 2H), 1.26-1.17 (m, 1H).
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 187.0, 131.9, 120.4, 57.4, 49.1, 42.3, 29.6, 25.5, 25.4.
HRMS (ESI) *m/z* calcd for $[C_{11}H_{19}O_2N_2S]^+$ $[M + H]^+$: 243.1162, found 243.1164.

1'-allyl-1',5',6',6a'-tetrahydrospiro[cyclopentane-1,4'-cyclopenta[c][1,2,5]thiadiazole] 2',2'-dioxide (3z)



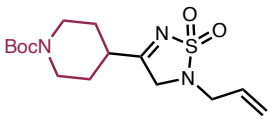
Yield: 85 mg, 71% (0.52 mmol scale), clear oil. (15 mg, 23% recovered SM)
New compound
^{1}H NMR (400 MHz, $CDCl_3$) $^{z}\delta$ 5.93 (dddd, *J* = 17.3, 10.0, 7.5, 5.9 Hz, 1H), 5.37 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.32 – 5.24 (ap. m, 1H), 4.10 – 3.94 (m, 2H), 3.59 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.33 – 2.23 (m, 1H), 2.12 – 1.96 (m, 4H), 1.95 – 1.83 (m, 3H), 1.80 – 1.70 (m, 3H), 1.70 – 1.62 (m, 2H), 1.57 – 1.45 (m, 1H).
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 199.6, 132.6, 120.3, 69.6, 49.7, 49.5, 40.0, 39.8, 37.5, 30.0, 25.5, 25.2.
HRMS (ESI) *m/z* calcd for $[C_{12}H_{19}O_2N_2S]^+$ 255.1162 found: 255.163

2-allyl-4-(2-(2,6,6-trimethylcyclohex-2-en-1-yl)ethyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3aa)



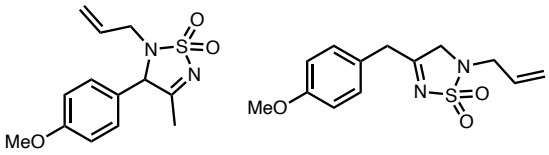
Yield: 36 mg mg, 70% (0.36 mmol scale), pale yellow solid. (18 mg, 26% recovered SM)
New compound
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (ddt, *J* = 16.6, 10.1, 6.5 Hz, 1H), 5.42 – 5.25 (m, 3H), 4.05 (s, 1H), 3.80 (d, *J* = 6.5 Hz, 2H), 2.66 – 2.45 (m, 2H), 2.06 – 1.83 (m, 3H), 1.83 – 1.69 (m, 1H), 1.69 – 1.64 (m, 3H), 1.55 (s, 1H), 1.43 – 1.30 (m, 1H), 1.27 – 1.11 (m, 1H), 0.93 (s, 3H), 0.88 (d, *J* = 3.5 Hz, 3H).
^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 183.9, 134.7, 132.0, 122.0, 120.4, 59.0, 49.2, 48.4, 33.4, 32.7, 31.6, 27.8, 27.7, 26.0, 23.6, 23.0.

tert-butyl 4-(5-allyl-1,1-dioxido-4,5-dihydro-1,2,5-thiadiazol-3-yl)piperidine-1-carboxylate (3ab)



Yield: 75 mg, 58% (0.41 mmol scale), yellow waxy solid. (35 mg, 41% recovered SM)
New compound

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 5.88 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H), 5.38 – 5.26 (m, 2H), 4.08 (s, 2H), 3.79 (d, *J* = 6.5 Hz, 2H), 2.80 (t, *J* = 12.3 Hz, 3H), 2.63 (tt, *J* = 11.5, 3.7 Hz, 1H), 1.91 (d, *J* = 13.0 Hz, 3H), 1.62 (qd, *J* = 11.9, 4.3 Hz, 4H), 1.44 (s, 9H).
^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 185.0, 154.6, 131.8, 120.7, 80.1, 57.2, 49.2, 40.6, 28.5, 28.5.
HRMS (ESI) *m/z* calcd for $[C_{15}H_{25}N_3O_4NaS]^+$ 366.1458 found: 366.1459



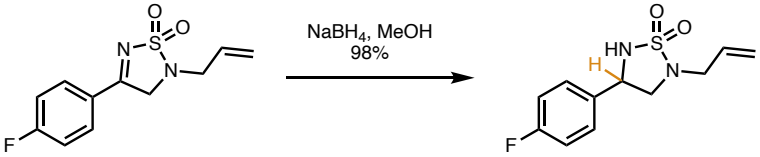
To a flame dried 20 mL vial equipped with a stir bar qnd charged with 100 mg of 3Å MS was added 4-methoxyphenylacetone (50.0 mg, 0.31 mmol, 1.0 equiv), allylamine (87 mg, 1.52 mmol, 5.0 equiv) and cyclohexane (1.5 mL). the vial was capped with a teflon cap and the reaction mixture was heated to 60 °C for 24 hours. At this point, the volatiles were removed under vacuum and the vial was capped with a septum cap and put under an atmosphere of nitrogen gas. The vial was cooled to 0 °C and **A** (118 mg, 0.34 mmol, 1.1 equiv) was added as a solution in acetonitrile (1.5 mL). The cooling bath was removed and after stirring for 3 hours, ditertbutylpyridine (58 mg, 0.31 mmol, 1.0 equiv) was added. After a further two hours, the mixture was filtered through silica and concentrated. Purification of the crude mixture by column chromatography eluting with 4:1 hexanes:EtOAc gave **11** (45 mg, 53%) as a pale pink oil and **12** (10 mg, 12%) as a clear oil.

11:
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 2H), 6.96 – 6.90 (m, 2H), 5.79 (dddd, *J* = 17.1, 10.1, 8.1, 5.1 Hz, 1H), 5.21 – 5.11 (m, 2H), 5.01 (s, 1H), 3.98 – 3.87 (m, 2H), 3.82 (s, 3H), 3.43 (dd, *J* = 15.2, 8.0 Hz, 1H), 2.07 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 182.3, 160.7, 131.6, 129.4, 124.5, 120.3, 115.2, 115.0, 73.1, 55.4, 45.9, 18.9.

12:
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.84 – 6.81 (m, 3H), 5.82 – 5.71 (m, 3H), 5.26 – 5.14 (m, 4H), 3.87 (s, 2H), 3.78 (s, 2H), 3.74 (s, 3H), 3.68 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 182.0, 159.5, 131.7, 130.3, 124.2, 120.4, 114.8, 57.9, 55.4, 49.1, 39.3.

HRMS (ESI) *m/z* calcd for $[C_{13}H_{17}N_2O_3S]^+$ 281.0954 found: 281.0955

4. Post-synthetic modifications and their characterization data



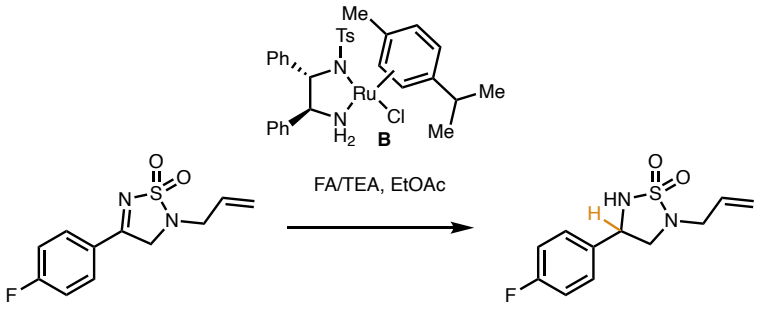
13: To a flame-dried 2 dram vial equipped with a stir bar and septum cap was added **3a** (68.0 mg, 0.27 mmol, 1.0 equiv) and $NaBH_4$ (30.3 mg, 0.80 mmol, 3 equiv). Anhydrous methanol (1.3 mL) was added through the septum and the reaction mixture was stirred for 1 h at which point the solution was poured into a separatory funnel containing water (4 mL). The aqueous layer was washed with EtOAc (3 x 4 mL), and the combined organic layers were dried with magnesium sulfate, filtered, and concentrated to give **13** (67 mg, 0.26 mmol, 97%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (ddt, J = 8.2, 5.0, 2.5 Hz, 2H), 7.11-7.04 (m, 2H), 5.94-5.84 (m, 1H), 5.33 (dt, J = 17.1, 1.3 Hz, 1H), 5.28 (dd, J = 10.1, 1.1 Hz, 1H), 4.82 (q, J = 7.2 Hz, 1H), 4.64 (d, J = 5.9 Hz, 1H), 3.79 (ddt, J = 14.1, 6.1, 1.3 Hz, 1H), 3.71 (dd, J = 9.8, 7.2 Hz, 1H), 3.54 (dd, J = 14.1, 7.0 Hz, 1H), 3.15 (dd, J = 9.8, 8.2 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 162.9 (d, J = 248 Hz), 134.3 (d, J = 3 Hz), 131.7, 128.3 (d, J = 8 Hz), 120.2, 116.1 (d, J = 21.6 Hz), 55.32, 55.27, 49.5

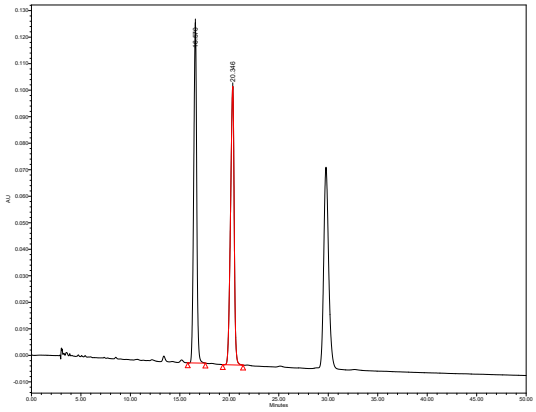
^{19}F NMR (376 MHz, $CDCl_3$) δ -112.6 - -112.7 (m).

HRMS (ESI) *m/z* calcd for $[C_{11}H_{14}FN_2O_2S]^+$ $[M+H]^+$: 257.0755, found 257.0765.



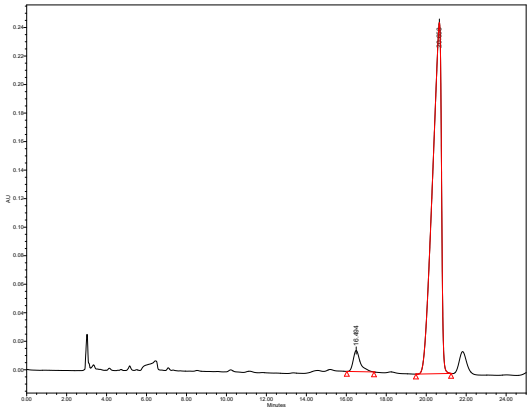
13: A flame-dried 5 mL microwave vial was charged with **3a** (20 mg, 0.079 mmol, 1.0 equiv) and ruthenium complex **B** (1.25 mg, 1.96 µmol, 2.5 mol %). The vial was capped with a septum and EtOAc (0.39 mL) was added. The mixture was cooled to 0 °C before an azeotropic mixture of formic acid/triethylamine (~5:2, 0.033 mL, 0.55 mmol, 7 equiv) was added through a syringe. The mixture was stirred for 24 h before being filtered through a short silica plug and concentrated to give **13** (19 mg, 0.074 mmol, 94%) as a white solid. Chiral HPLC analysis (Chiralcel AD–3 column in 8% IPA in hexanes) indicated an enantiomeric excess of 91%.

Figure S1. HPLC trace of Rac-**13**

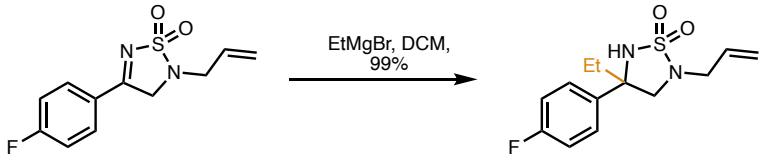


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.570	2701276	50.09	128240	BB			Unknown	
2		20.346	2691144	49.91	104846	BB			Unknown	

Figure S2: HPLC trace of enantioenriched **13**



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.494	365694	4.56	14786	bb			Unknown	
2		20.658	7653831	95.44	246165	bb			Unknown	



14: A flame-dried 1 dram vial equipped with a stir bar was charged with **3a** (26.0 mg, 0.10 mmol. 1.0 equiv). The vial was evacuated and backfilled with nitrogen three times before anhydrous THF (1.0 mL) was added and the mixture was cooled to 0 °C. Ethyl magnesium bromide (3M in THF, 0.05 mL, 0.15 mmol, 1.5 equiv) was added slowly and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. After TLC indicated completion of the reaction, the mixture was quenched with water (5 mL) and the aqueous layer

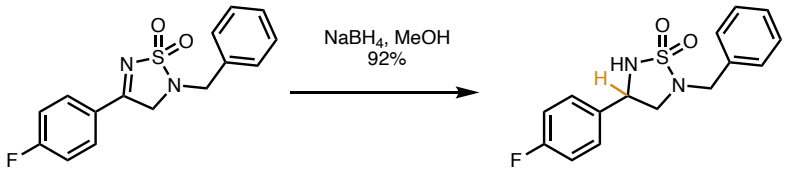
was extracted with EtOAc (3 x 5 mL). The combined organic extracts were dried with $MgSO_4$ and concentrated to give **14** (29.0 mg, 0.1 mmol. 99%) as a clear oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (ddd, J = 8.8, 5.2, 2.6 Hz, 2H), 7.11-7.02 (m, 2H), 5.82 (ddt, J = 17.0, 10.1, 6.4 Hz, 1H), 5.30 – 5.21 (m, 2H), 4.54 (s, 1H), 3.74 (dd, J = 14.3, 5.9 Hz, 1H), 3.60 (d, J = 9.6 Hz, 1H), 3.44 (dd, J = 14.3, 6.9 Hz, 1H), 3.36 (d, J = 9.6 Hz, 1H), 2.14 (dq, J = 14.7, 7.4 Hz, 1H), 2.03 (dq, J = 14.8, 7.5 Hz, 1H), 0.80 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.2 (d, J = 247 Hz), 137.9 (d, J = 3 Hz), 132.0, 127.3 (d, J = 8 Hz), 119.8, 115.6 (d, J = 22 Hz), 63.8, 60.1, 49.1, 34.8, 8.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.7 - -114.8 (m).

HRMS (ESI) *m/z* calcd for $[C_{13}H_{18}O_2N_2FS]^+$ $[M+H]^+$: 285.1068, found 285.1079.



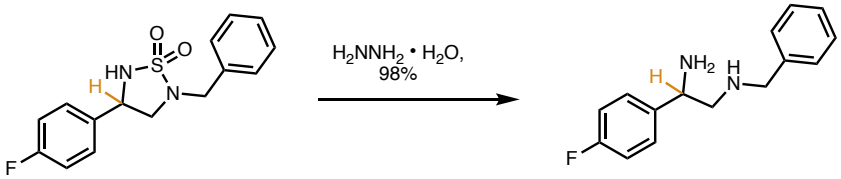
S1: To a flame-dried 1 dram vial equipped with a stir bar and septum cap was added **3f** (40.0 mg, 0.13 mmol, 1.0 equiv) and $NaBH_4$ (14.9 mg, 0.39 mmol, 3 equiv). Anhydrous methanol (0.66 mL) was added through the septum and the reaction mixture was stirred for 1 h at which point the solution was poured into a separatory funnel containing water (4 mL). The aqueous layer was washed with EtOAc (3 x 4 mL), and the combined organic layers were dried with magnesium sulfate, filtered, and concentrated to give **S1** (40.3 mg, 0.12 mmol, 92%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.30 (m, 7H), 7.07-7.02 (m, 2H), 4.78 (q, J = 7.2 Hz, 1H), 4.70 (d, J = 6.3 Hz, 1H), 4.38 (d, J = 13.5 Hz, 1H), 3.98 (d, J = 13.5 Hz, 1H), 3.55 (dd, J = 9.7, 7.2 Hz, 1H), 3.07 (dd, J = 9.7, 8.2 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 162.8 (d, J = 248 Hz), 134.7, 134.3 (d, J = 3 Hz), 128.8, 128.7, 128.31, 128.25 (d, J = 8 Hz), 116.0 (d, J = 22 Hz), 55.3, 55.1, 50.5.

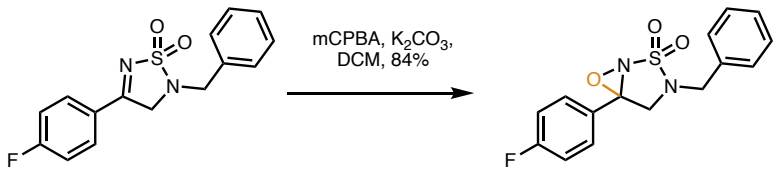
^{19}F NMR (376 MHz, $CDCl_3$) δ -112.6 - -112.7 (m).

HRMS (ESI) *m/z* calcd for $[C_{15}H_{16}FN_2O_2S]^+$ $[M+H]^+$: 307.0911, found 307.0920.



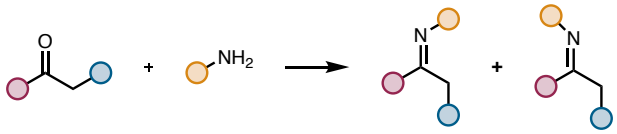
15: A 5 mL microwave vial equipped with a stir bar was charged with **S1** (10.0 mg, 0.03 mmol, 1.0 equiv). The vial was capped with a pressure cap and hydrazine hydrate (0.33 mL) was added to make a 0.1 M solution. The reaction mixture was heated to 110 °C for 12 h before being cooled and concentrated. The crude residue was left under high vacuum (<300 mtorr) for several days to remove residual hydrazine and yield **15 (**7.8 mg, 0.03 mmol, 98%) as a light yellow oil.

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.33-7.28 (m, 5H), 7.26-7.23 (m, 2H), 7.03-6.99 (m, 2H), 4.04 (dd, J = 8.2, 4.8 Hz, 1H), 3.83-3.78 (m, 2H), 2.83-2.80 (m, 1H), 2.73-2.70 (m, 1H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.0 (d, J = 245 Hz), 140.3, 128.6, 128.4, 128.1, 128.0 (d, J = 8 Hz), 126.4, 115.3 (d, J = 21 Hz), 57.2, 55.0, 53.9.
^{19}F NMR (565 MHz, $CDCl_3$) δ -113.87 (s)
HRMS (ESI) *m/z* calcd for $[C_{15}H_{18}N_2F]^+$ $[M+H]^+$: 245.1449, found 245.1458.



16: To a 20 mL vial equipped with a stir bar was added **3f** (35.0 mg, 0.12 mmol, 1.0 equiv) followed by DCM (1.7 mL) and saturated aqueous potassium carbonate (1.7 mL). To this mixture was added dropwise a solution of *m*-CPBA (95%, 31.0 mg, 0.17 mmol, 1.5 equiv) in DCM (1.2 mL). After TLC indicated completion of the reaction, the mixture was poured into a separatory funnel and the layers separated. The organic layer was washed with saturated aqueous $NaSO_3$ (5 mL), saturated $NaHCO_3$ (5 mL) and brine (5 mL), and then dried with $MgSO_4$ and concentrated to give **16** (31.0 mg, 0.097 mmol, 84%) as a white solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45-7.35 (m, 7H), 7.13 (t, J = 8.3 Hz, 2H), 4.89 (d, J = 14.7 Hz, 1H), 4.19 (d, J = 14.7 Hz, 1H), 4.08-3.97(m, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.5 (d, J = 253 Hz), 135.3, 129.5 (d, J = 9 Hz), 129.0, 128.5, 128.2, 124.7 (d, J = 3 Hz), 116.3 (d, J = 22 Hz), 82.8, 57.5, 49.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -107.3 - -107.4 (m).
HRMS (ESI) *m/z* calcd for $[C_{15}H_{14}O_3N_2FS]^+$ $[M+H]^+$: 321.0704, found 321.0712.

5. Imine formation studies:



To a flame dried 1 dram vial equipped with a stir bar was added activated mol sieves (2 mg per mg of ketone). The vial was capped with a septum cap and evacuated followed by backfilling with dry nitrogen gas. CyH was added (for a concentration of 0.2 M) followed by ketone (1.0 equiv) and amine (1.1 equiv). The septum cap was replaced with a teflon lined cap and the reaction mixture was heated to 60 °C. After 24 hours, an aliquot was removed. The volatiles were removed under reduced pressure and the crude residue was analyzed by 1H NMR.

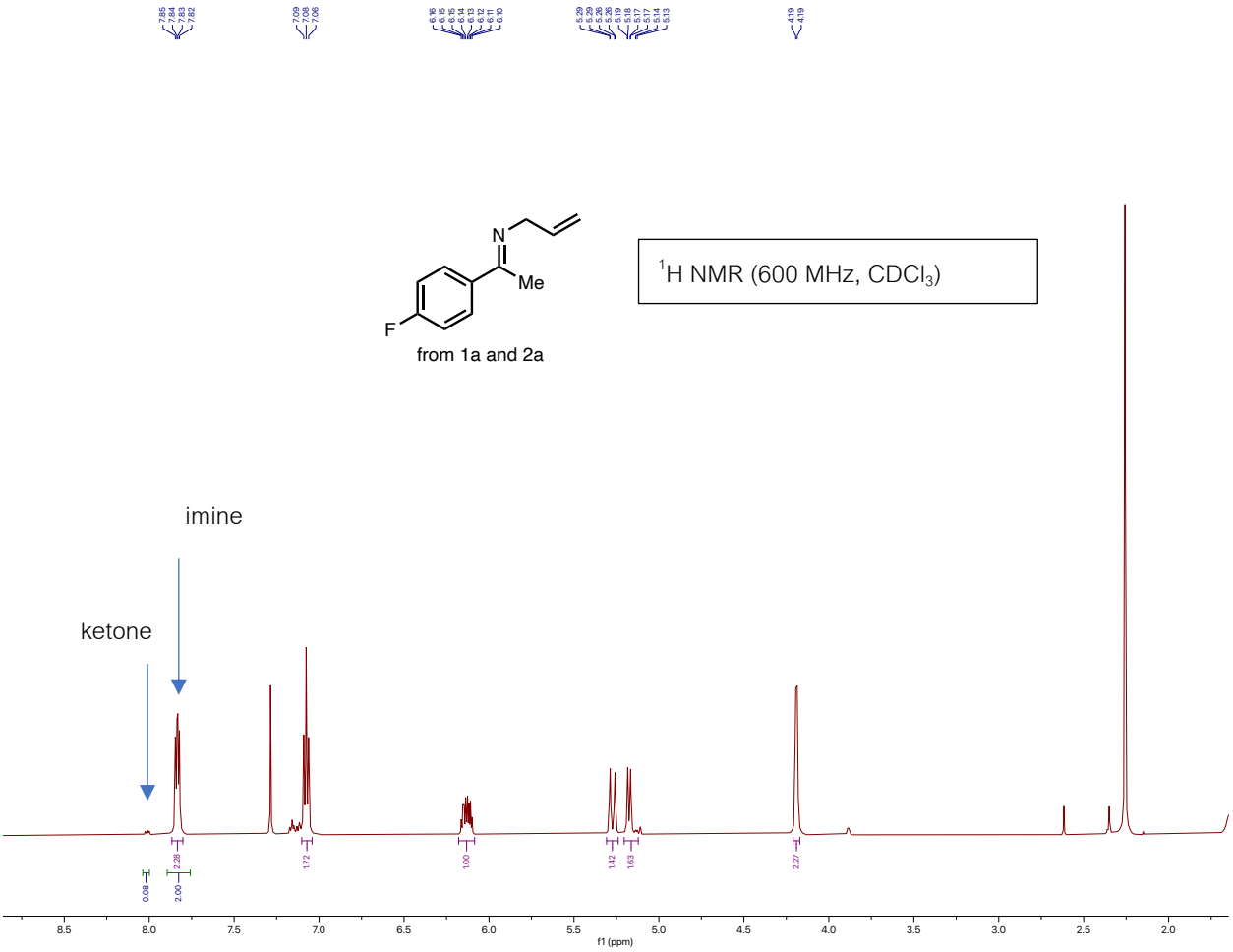


Figure S3: NMR showing ratio of imine 4a to ketone 1a

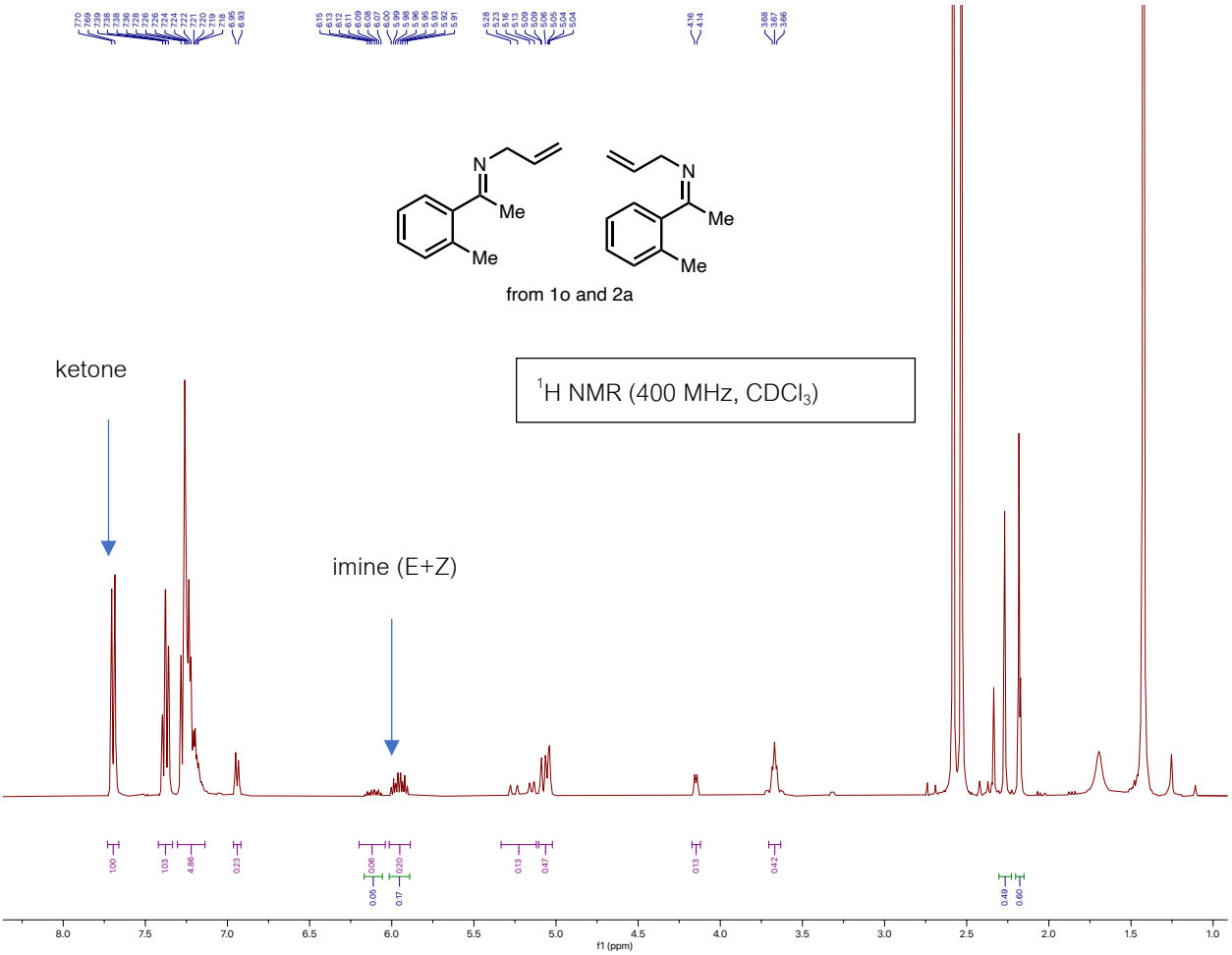


Figure S4: NMR showing ratio of imine 4o to ketone 1o

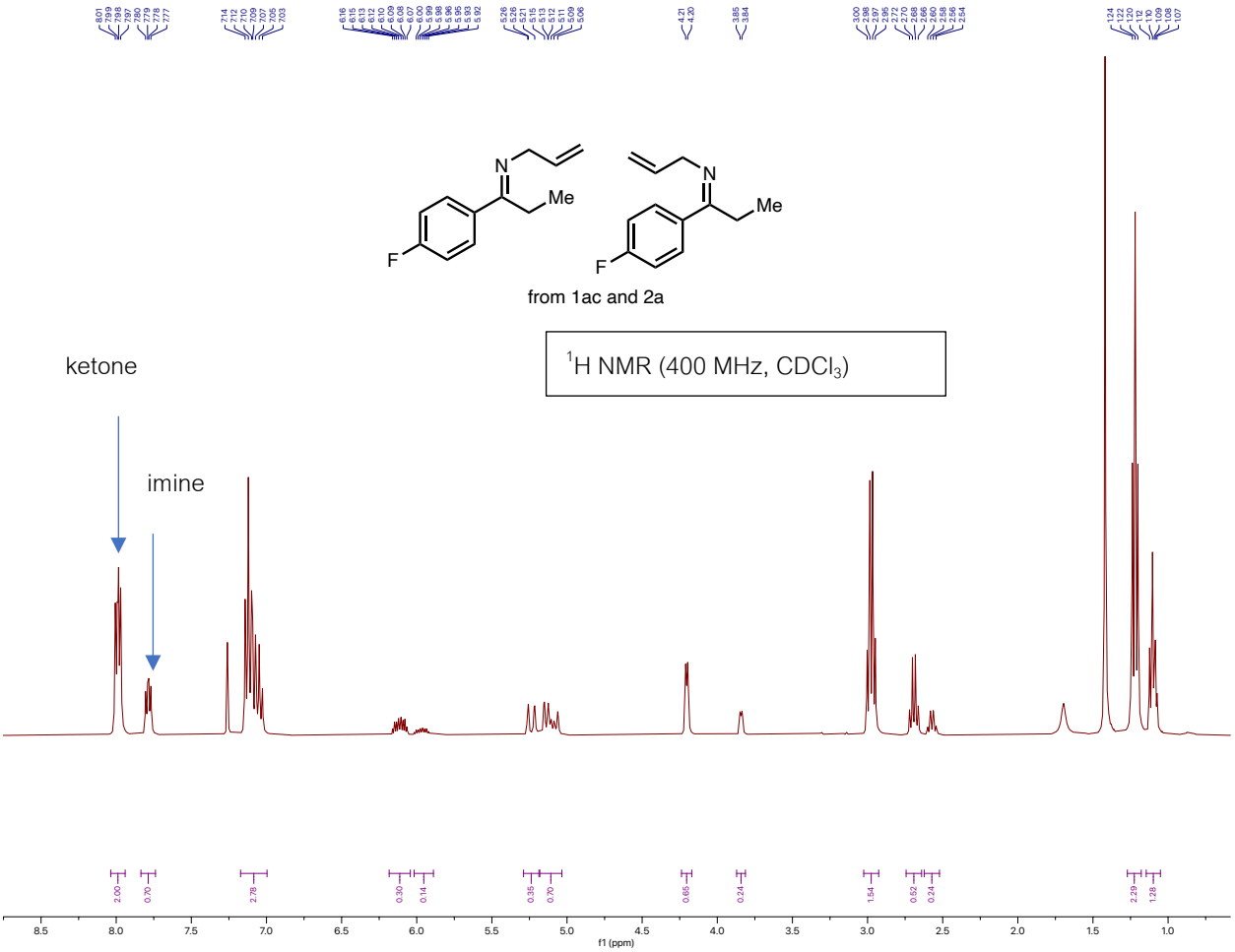


Figure S5: NMR showing ratio of imine 4ac to ketone 1ac

After analysis of the aliquot, the above mixture was concentrated and cooled to 0 °C. A (1.1 equiv) in MeCN (equal to the amount of CyH used) was added slowly. The mixture was warmed to r.t. and stirred for 3 hours before ditertutylpyridine (1.0 equiv) was added. After a further 2 hours, the reaction mixture was filtered through silica and concentrated. NMR analysis of the crude residue indicated no conversion to **3ac**.

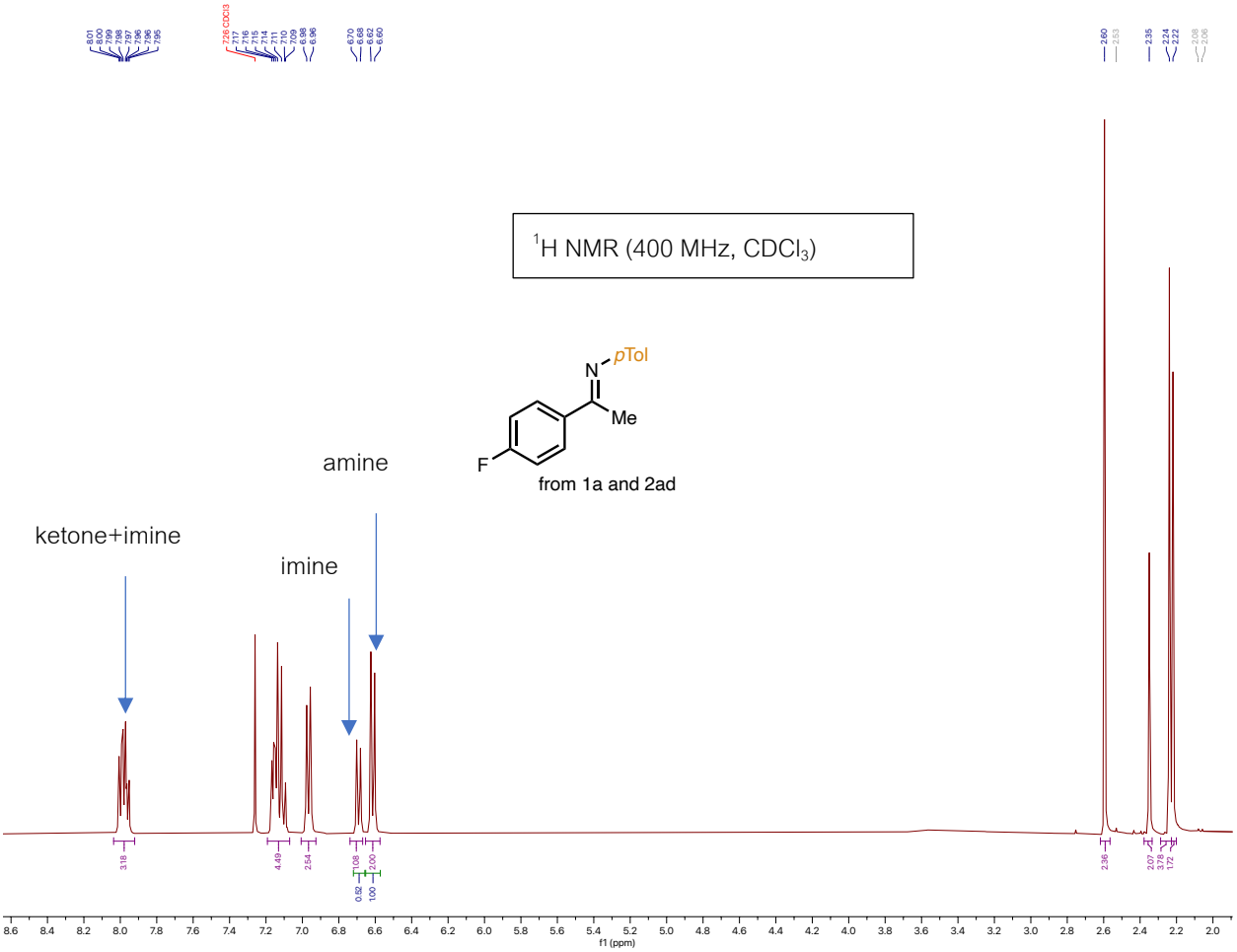
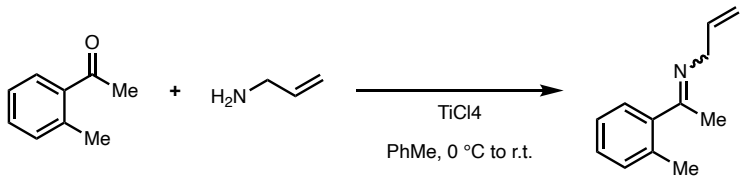


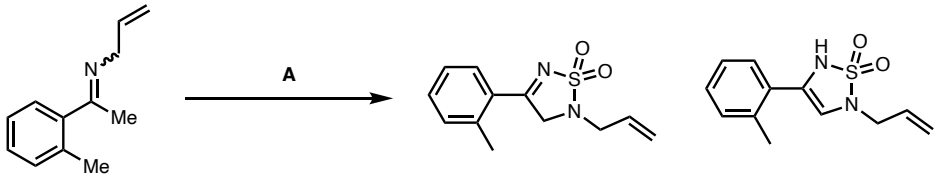
Figure S6: NMR showing ratio of imine 4ad to ketone 1a

After analysis of the aliquot, the above mixture was concentrated and cooled to 0 °C. A (1.1 equiv) in MeCN (equal to the amount of CyH used) was added slowly. The mixture was warmed to r.t. and stirred for 3 hours before ditertutylpyridine (1.0 equiv) was added. After a further 2 hours, the reaction mixture was filtered through silica and concentrated. NMR analysis of the crude residue indicated no conversion to **3ad**.



4o: Prepared according to the method of Chen *et al.*[3] To a flame dried 50 mL round-bottomed-flask equipped with a stir bar was added ketone **1o** (196 µL, 1.49 mmol, 1.0 equiv) and amine **2a** (560 µL, 7.45 mmol, 5 equiv.) and toluene (14.9 mL). The reaction mixture was cooled to 0 °C

and then $TiCl_4$ (1 M in DCM, 954 μL, 954 μmol, 0.64 equiv) was added dropwise over ten minutes. Upon complete addition, the mixture was allowed to warm to room temperature and was stirred for 2 hours. After that time, the mixture was filtered through celite eluting with EtOAc. The filtrate was washed with brine, dried with Na_2SO_4 and concentrated to yield the imine as a colorless oil. Spectral data was in agreement with those reported.[3] The imine was used directly in the following reaction.



A flame dried 20 mL vial equipped with a stir bar and septum cap was charged with **4o** (57 mg, 0.33 mmol, 1.0 equiv) and the vial was evacuated/backfilled with nitrogen gas, and then cooled to 0 °C. In a seperate flame dried one dram vial was added **A** (130 mg, 0.36 mmol, 1.1 equiv). MeCN (1.6 mL) was then added to the one dram vial and the corresponding solution was slowly added to the vial containing **4o**. The reaction mixture was allowed to warm to r.t. and stirred for 3 hours after which time 2,6-di-tert-butylpyridine (0.078 mL, 0.36 mmol, 1.1 equiv) was added and the reaction stirred for a further 2 hours. The reaction mixture was then filtered through silica and concentrated to give a crude oil which was purified by flash column chromatography in 3:1 hexanes:EtOAc to give **3o** as a 5:1 mixture of tautomers favoring the enamine form. Spectral data for the enamine tautomer is given below:

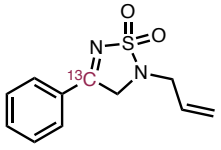
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.33 – 7.24 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 5.91 (ddt, *J* = 16.5, 11.2, 5.8 Hz, 1H), 5.18 (d, *J* = 10.3 Hz, 1H), 4.98 (d, *J* = 17.1 Hz, 1H), 4.78 (d, *J* = 5.8 Hz, 2H), 2.16 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 136.6, 133.6, 131.6, 130.6, 130.3, 129.9, 126.5, 126.0, 119.1, 50.3, 20.0.

6. Isotopic labeling experiments

2-allyl-4-phenyl-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (^{13}C-3l)

Prepared according to the representative procedure using commercially available acetophenone-α-^{13}C.



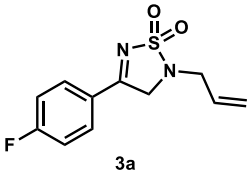
^{13}C-3l:

Yield: 50 mg, 51% (0.45 mmol scale), white solid

^{1}H NMR (600 MHz, $CDCl_3$) *δ* 7.92-7.90 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 6.00-5.92 (m, 1H), 5.41 (dd, *J* = 17.1, 1.3 Hz, 1H), 5.34 (dd, *J* = 10.1, 1.1 Hz, 1H), 4.58 (d, *J* = 5.1 Hz, 2H), 3.90 (d, *J* = 6.5 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 174.8, 134.9, 131.9, 129.3 (d, J = 4.5 Hz), 129.0, 128.5 (d, J = 2.7 Hz), 120.5, 56.3 (d, J = 33.5 Hz), 49.2 (d, J = 3.0 Hz).
HRMS (ESI) *m/z* calcd for $[C_{10}{}^{13}CH_{13}O_2N_2S]^+$ $[M + H]^+$: 238.0726, found 238.0733.

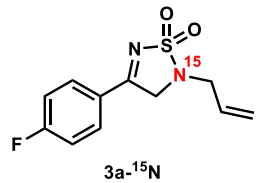
2-allyl-4-(4-fluorophenyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3a)
A ^{15}N-NMR of unlabeled **3a** was obtained by making a saturated solution of **3a** in 0.5 mL of $CDCl_3$ and running the ^{15}N NMR experiment overnight. The two nitrogen peaks observed were assigned by comparison to literature examples.[4, 5]



3a

^{15}N NMR (61 MHz, $CDCl_3$) δ 299.34, 85.73.

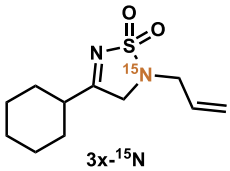
2-allyl-4-(4-fluorophenyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide-2-^{15}*N* (3a-^{15}N)
Prepared according to the representative procedure using commercially available ^{15}N-allylamine.



3a-^{15}N

Yield: 23.4 mg, 64% (0.14 mmol scale) yellow solid
^{15}N NMR (61 MHz, $CDCl_3$) δ 85.73.
HRMS (ESI) *m/z* calcd for $[C_{11}H_{12}FN^{15}NO^2S]^+$ $[M + H]^+$: 256.0568, found 256.0571.

2-allyl-4-cyclohexyl-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide-2-^{15}*N* (3x-^{15}N)
Prepared according to the representative procedure using commercially available ^{15}N-allylamine.

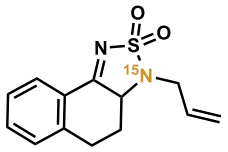


3x-^{15}N

Yield: 25 mg, 52% yield (0.22 mmol scale) white solid
^{15}N NMR (61 MHz, $CDCl_3$) δ 85.52.
HRMS (ESI) *m/z* calcd for $[C_{11}H_{19}O_2N^{15}NS]^+$ $[M + H]^+$: 244.1132, found 244.1143.

3-allyl-3,3a,4,5-tetrahydronaphtho[1,2-c][1,2,5]thiadiazole 2,2-dioxide (3w-^{15}N)
Prepared according to the general procedure using commercially available ^{15}N-allylamine.

Yield: 5.0 mg, 10% (0.19 mmol scale), yellow oil from α-tetralone



3w-^{15}N

Yield: 14.0 mg, 26% (0.22 mmol scale), yellow oil from β-tetralone

^{15}N NMR (61 MHz, $CDCl_3$) δ 101.04.

HRMS (ESI) *m/z* calcd for $[C_{13}H_{15}O_2N^{15}NS]^+$ $[M + H]^+$: 264.0819, found 264.0827.

7. Computational Methods

Structure optimizations, coordinate scans and transition structure searches were performed in the gas phase using restricted (in case of closed shell systems) or unrestricted (in case of open shell systems) DFT (B3LYP-D3/6-31G+*) in Schrödinger Jaguar. Vibrational analysis using the analytic Hessian was performed for the gas-phase geometries, and stationary points were confirmed by either having no or exactly one (in case of transition states) imaginary frequency. Entropies and solvent contributions were ignored for the purpose of this analysis. Calculated energies are summarized in Table S1 and the cartesian coordinates of structures in the favored pathway are tabulated below.

Table S1. Calculated Energies

STRUCTURE	H (AT 298.15 K; KCAL/MOL)
5	-762769.2850

TS2	-762734.6336
TS1	-762731.0389
6c	-694026.9856
6b	-694031.1968
6a	-694035.9236
7	-762767.5060
TS3a	-694007.0768
TS3c	-694017.9586
TS3b	-694025.4696
TS4	-762738.0469
8	-694069.9463
TS5	-694018.9578
9	-694107.8830
N_2	-68725.31142

Cartesian Coordinates

5

C	2.50080	0.19770	-3.00230
C	1.95920	-0.53650	-4.05130
C	0.59200	-0.59650	-4.29170
C	-0.26060	0.11660	-3.44950
C	0.24850	0.88120	-2.38790
C	1.63510	0.90030	-2.16730
C	-0.66470	1.66470	-1.52130
C	-1.74300	2.32000	-1.98560
N	-0.29530	1.74870	-0.12760
S	-0.48520	0.31150	0.75160
N	-2.24490	0.06880	0.73830
O	0.12430	-0.78400	0.01260
O	-0.18020	0.60160	2.14060
N	-2.61970	-0.60830	-0.23860
N	-3.04920	-1.23060	-1.08650
C	-0.68010	2.95930	0.62760
F	2.79670	-1.23110	-4.86430
H	3.57490	0.20590	-2.84800
H	0.21320	-1.20410	-5.10700
H	-1.33440	0.05040	-3.59930
H	2.03490	1.46660	-1.33210
H	-2.42490	2.85570	-1.33500
H	-1.94700	2.35280	-3.05010
H	-1.74970	2.98570	0.87050
H	-0.10300	2.99460	1.55130
H	-0.42580	3.81660	0.00170

TS2

S	-0.89010	1.62820	-0.04370
N	0.27310	0.40210	-0.14660
C	0.16070	-0.44010	-1.35280
N	-1.77530	1.07130	-1.48940
C	-0.43110	-1.60230	-1.20950
N	-2.79960	-1.02300	-1.16120
N	-2.49280	0.08290	-1.23740
O	-1.72330	1.47750	1.14390
O	-0.33850	2.93530	-0.38490
C	1.63780	0.74380	0.29150
C	0.85830	-0.00470	-2.59120
C	1.05020	1.33010	-2.99240
C	1.82630	1.63420	-4.11180
C	2.39980	0.59140	-4.82950
C	2.23520	-0.73770	-4.46750
C	1.47240	-1.02200	-3.34060
F	3.15740	0.87760	-5.91960
H	-0.62300	-2.28410	-2.04200
H	-0.79780	-1.94160	-0.20600
H	2.20180	-0.19230	0.31000
H	2.13060	1.45470	-0.38140
H	1.60670	1.15520	1.30380
H	0.59760	2.14380	-2.43760
H	1.98230	2.65940	-4.43190
H	2.71580	-1.52100	-5.04460
H	1.38590	-2.05280	-3.01340

TS1

C	2.58770	0.22720	-3.04420
C	2.09470	-0.49040	-4.12790
C	0.73650	-0.57820	-4.40730

C	-0.15610	0.08850	-3.56860
C	0.30210	0.83360	-2.47110
C	1.68130	0.88220	-2.21300
C	-0.65460	1.56830	-1.60790
C	-1.74050	2.20190	-2.08860
N	-0.32140	1.64080	-0.20750
S	-0.51730	0.18340	0.65400
N	-2.06980	-0.01570	1.14270
O	0.08390	-0.87280	-0.14470
O	-0.12480	0.46310	2.05740
N	-3.03400	-0.50230	-0.42960
N	-3.87810	-0.93440	-1.00150
C	-0.76000	2.82860	0.55150
F	2.97170	-1.14010	-4.93730
H	3.65670	0.25910	-2.86030
H	0.39530	-1.17050	-5.25010
H	-1.22320	0.00170	-3.75230
H	2.04240	1.43350	-1.35070
H	-2.44850	2.71170	-1.44480
H	-1.91910	2.25310	-3.15690
H	-1.83350	2.81420	0.77770
H	-0.20230	2.87060	1.48690
H	-0.52240	3.70380	-0.05590

7

S	-0.72110	1.65470	0.01640
N	0.30610	0.28240	-0.11420
C	-0.27520	-0.10450	-1.45220
N	-1.43920	0.83540	-1.38000
C	-0.98820	-1.46680	-1.41010
N	-2.39650	-1.14990	-1.08550
N	-2.61240	0.06600	-1.03430
O	-1.55500	1.65010	1.20540
O	-0.05710	2.88160	-0.41600
C	1.74600	0.46880	0.08000
C	0.63920	0.12720	-2.63430
C	0.65690	1.35470	-3.30980
C	1.54660	1.57130	-4.36270
C	2.41810	0.54970	-4.71930
C	2.43410	-0.67790	-4.06780
C	1.53510	-0.88030	-3.02010
F	3.28410	0.75490	-5.74270
H	-0.97560	-1.97570	-2.37810
H	-0.60330	-2.14150	-0.64010
H	2.23600	-0.49510	-0.08090
H	2.17540	1.21570	-0.59820
H	1.91470	0.77170	1.11670
H	-0.02700	2.14240	-3.01460
H	1.56880	2.51250	-4.90220
H	3.13080	-1.44830	-4.38120
H	1.53910	-1.83670	-2.50240

TS4

S	-0.65250	1.78460	-0.01740
N	0.13680	0.20780	-0.06630
C	-0.43720	0.11490	-1.42120
N	-1.38210	1.16940	-1.38390
C	-0.90430	-1.17770	-1.94210
N	-2.50670	-1.42210	-0.66280
N	-2.97930	-0.46460	-0.32960

O	-1.53990	1.95240	1.13010
O	0.34370	2.83910	-0.27240
C	1.56220	0.13360	0.24080
C	0.56240	0.15810	-2.68010
C	0.32880	1.14740	-3.65570
C	1.21580	1.30940	-4.71240
C	2.32570	0.46830	-4.78880
C	2.58540	-0.51880	-3.84580
C	1.68770	-0.67730	-2.79110
F	3.18940	0.62560	-5.81480
H	-1.57060	-1.16890	-2.79910
H	-0.33860	-2.08680	-1.76920
H	1.89560	-0.90860	0.18930
H	2.18530	0.76210	-0.40830
H	1.68630	0.46710	1.27470
H	-0.52380	1.80610	-3.53140
H	1.07490	2.08400	-5.45920
H	3.46570	-1.14490	-3.94530
H	1.88430	-1.44660	-2.05260

8

S	-0.94480	1.38340	0.08850
N	0.45980	0.39500	-0.17230
C	-0.03960	0.08190	-1.54400
N	-1.38230	0.75500	-1.48540
C	-1.26000	-0.74510	-1.45260
O	-1.77270	0.91310	1.19150
O	-0.64620	2.80540	-0.06320
C	1.77340	1.01600	0.01250
C	0.85110	0.24520	-2.72030
C	1.00400	1.50720	-3.31080
C	1.87330	1.67980	-4.38740
C	2.58000	0.57450	-4.85010
C	2.45070	-0.69000	-4.28720
C	1.57490	-0.84780	-3.21140
F	3.42630	0.73510	-5.89820
H	-1.68160	-1.18480	-2.35290
H	-1.46850	-1.26160	-0.51840
H	2.52980	0.30480	-0.32970
H	1.88970	1.96250	-0.53000
H	1.91870	1.19060	1.08140
H	0.42950	2.34720	-2.93060
H	2.00500	2.64390	-4.86770
H	3.02020	-1.52100	-4.69000
H	1.45200	-1.82630	-2.75390

TS5

S	-2.69380	-0.10340	-0.58530
N	-1.11030	-0.82840	-0.28770
C	-0.94410	-0.94920	-1.75550
N	-2.20420	-0.32730	-2.16950
C	-1.17210	-2.39750	-1.82590
O	-3.77230	-0.97620	-0.11830
O	-2.70900	1.29300	-0.13500
C	-0.09150	-0.47330	0.68360
C	0.28940	-0.32910	-2.35880
C	1.38030	-1.08150	-2.80940
C	2.52210	-0.45260	-3.31430
C	2.54990	0.93450	-3.34880
C	1.48620	1.71530	-2.90440

C	0.35300	1.07370	-2.41250
F	3.65460	1.55220	-3.83540
H	-0.50800	-3.13740	-2.29000
H	-2.12410	-2.74020	-1.43050
H	0.83870	-0.97970	0.40760
H	0.08210	0.61040	0.69070
H	-0.40140	-0.80440	1.67780
H	1.36190	-2.16640	-2.78050
H	3.37270	-1.01960	-3.67790
H	1.55350	2.79730	-2.95300
H	-0.49750	1.65660	-2.07200

9

S	-2.38620	-0.01300	0.03880
N	-1.66070	-1.57610	0.02940
C	-0.48080	-0.20910	-1.50410
N	-1.47720	0.57680	-1.27920
C	-0.37130	-1.45260	-0.63030
O	-3.79570	-0.12160	-0.31200
O	-2.00340	0.73180	1.24320
C	-1.68480	-2.27040	1.31860
C	0.51440	0.10520	-2.53850
C	1.63310	-0.71980	-2.74880
C	2.57910	-0.40420	-3.72270
C	2.38590	0.74370	-4.48240
C	1.29100	1.58610	-4.30510
C	0.35750	1.26180	-3.32770
F	3.29830	1.05500	-5.43170
H	-0.17360	-2.34750	-1.23040
H	0.46260	-1.31730	0.08120
H	-1.35760	-3.30200	1.15750
H	-1.03820	-1.78910	2.06660
H	-2.71160	-2.29240	1.69260
H	1.78250	-1.61420	-2.15170
H	3.45000	-1.02690	-3.89790
H	1.18600	2.47110	-4.92400
H	-0.50470	1.89950	-3.16280

N2

N	0.00000	0.00000	0.55250
N	0.00000	0.00000	-0.55250

8. References

1. J.C. Culhane and V. V. Fokin. *Organic Letters*. 2011, **13**, 4578–4580.

2. C. Wang, X. Wu, L. Zhou and J. Sun, *Chem. - A Eur. J.*, 2008, **14**, 8789–8792

3. Z. Chen, B. Lu, Z. Ding, K. Gao and N. Yoshikai, *Org. Lett.*, 2013, **15**, 1966–1969.

4. ^{15}N NMR shifts reported herein are given in reference to NH_3 as per our spectrometer's defaults. To convert to the IUPAC standard nitromethane reference, one may subtract 380.2 ppm from the given chemical shift

5. J. Martin, M. L. Martin and J.-P. Gouesnard, *15N-NMR Spectroscopy*, Springer-Verlag, Berlin/Heidelberg/New York, 1981, vol. 18.

9. X-ray crystallographic information

Crystal structure of 4-(4-fluorophenyl)-2-(2-methylallyl)-2,3-dihydro-1,2,5-thiadiazole 1,1-dioxide (3b)

A colorless plate 0.13 x 0.09 x 0.02 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 1.00 seconds per frame at low angles and 4.00 seconds at high angles, using a scan width of 0.5°. Data collection was 100% complete to 74.000° in θ. A total of 13506 reflections were collected covering the indices -26<=h<=26, -6<=k<=7, -12<=l<=12. 2513 reflections were founded to be symmetry independent, with an R_{int} of 0.0571. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21/c (No. 14). The data were integrated using the CrysAlis^{Pro} 1.172.42.67a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

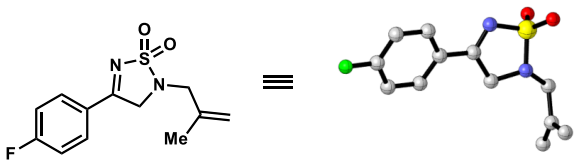


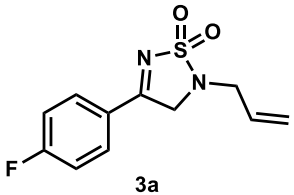
Figure S4. The X-ray Diffraction Configuration of **3b**.

Table 1. Crystal data and structure refinement for KPunjajom01_Sarpong.

Identification code	KPunjajom01_Sarpong
Empirical formula	C12 H13 F N2 O2 S
Formula weight	268.30

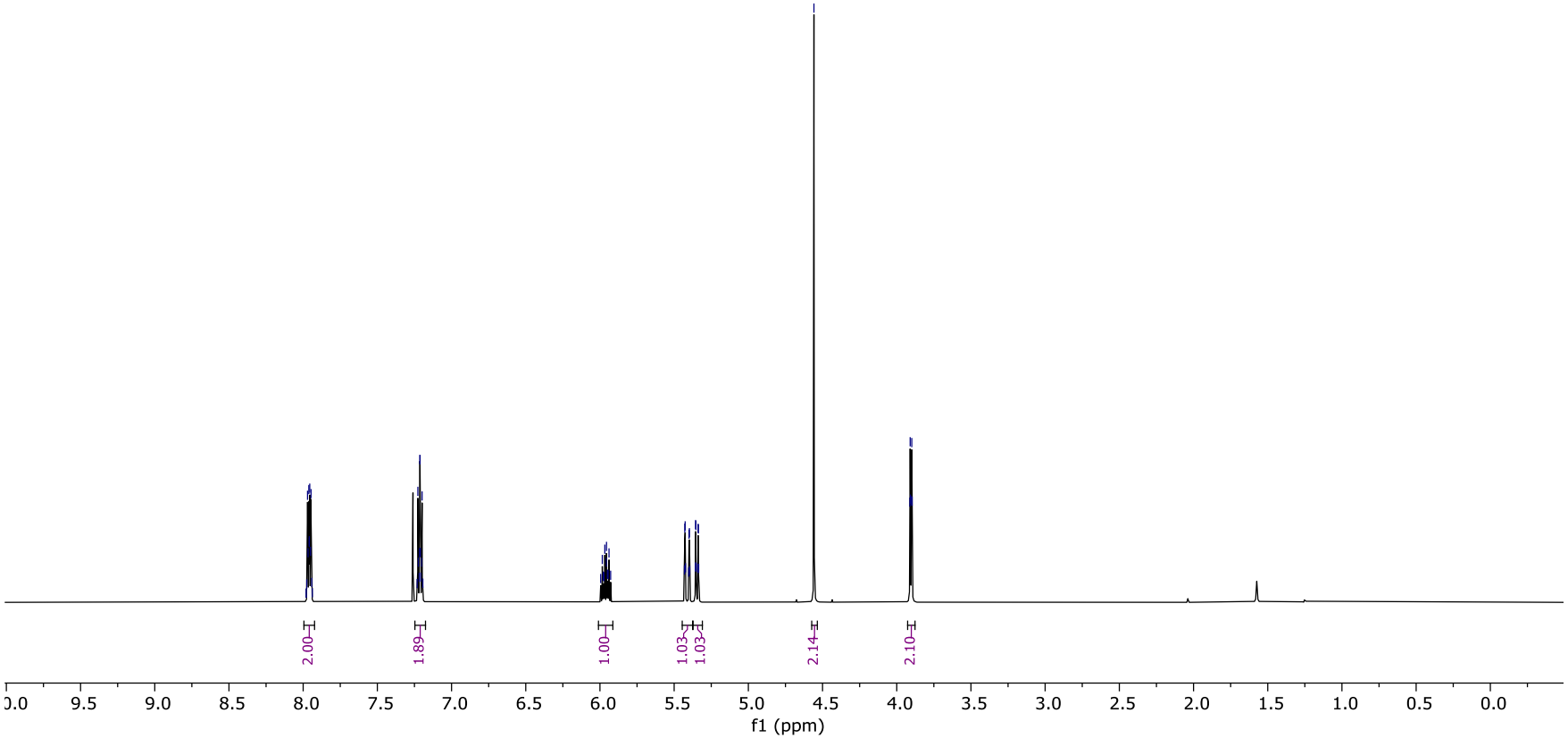
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 21.5943(5) Å a = 90°. b = 5.87350(10) Å b = 100.575(2)°. c = 9.8361(2) Å g = 90°.
Volume	1226.36(4) $Å^3$
Z	4
Density (calculated)	1.453 Mg/m^3
Absorption coefficient	2.449 mm^{-1}
F(000)	560
Crystal size	0.130 x 0.090 x 0.020 mm^3
Theta range for data collection	4.165 to 74.464°.
Index ranges	-26<=h<=26, -6<=k<=7, -12<=l<=12
Reflections collected	13506
Independent reflections	2513 [R(int) = 0.0571]
Completeness to theta = 74.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.85127
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2513 / 0 / 164
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.1052
R indices (all data)	R1 = 0.0448, wR2 = 0.1091
Extinction coefficient	n/a
Largest diff. peak and hole	0.280 and -0.440 $e.Å^{-3}$

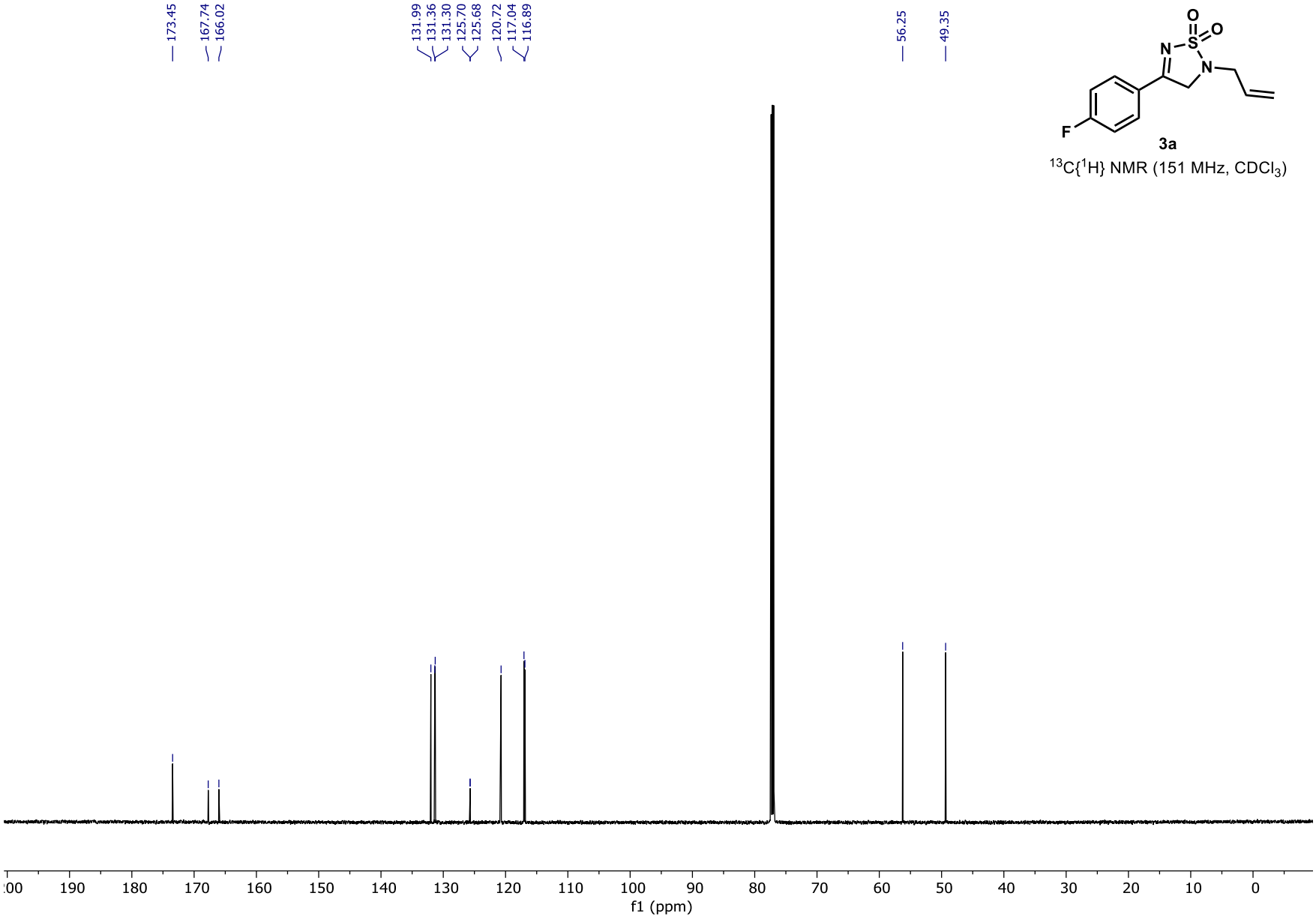
10. Copies of ^{1}H and ^{13}C NMR spectra for compounds

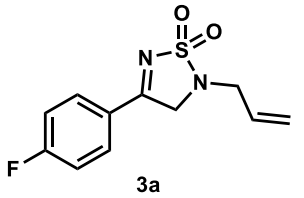


3a

^{1}H NMR (600 MHz, $CDCl_3$)

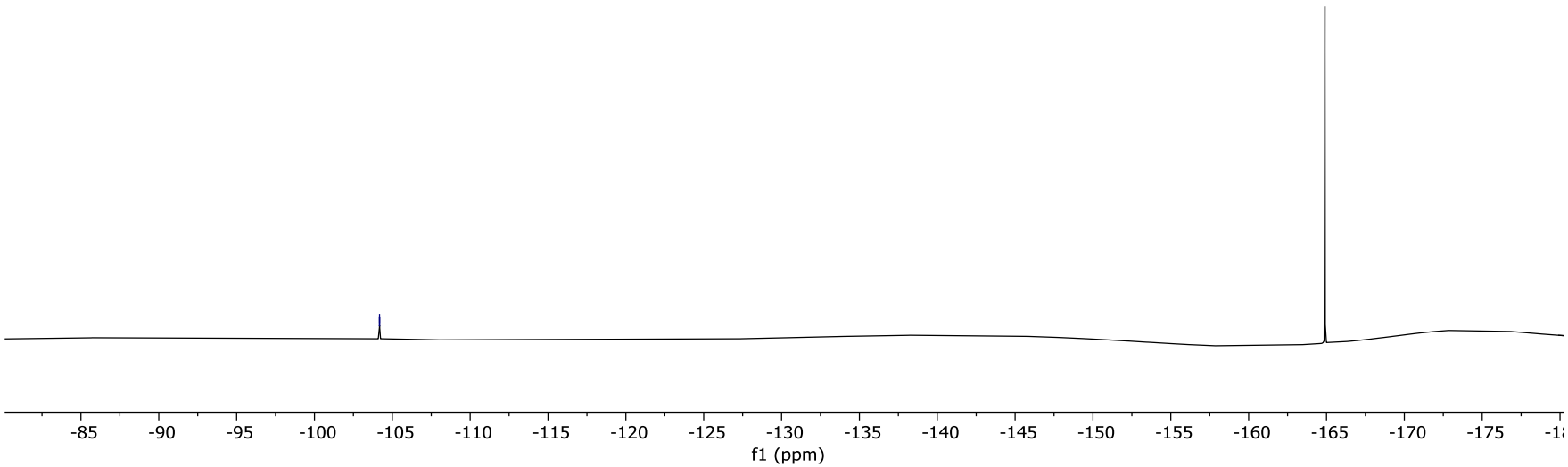


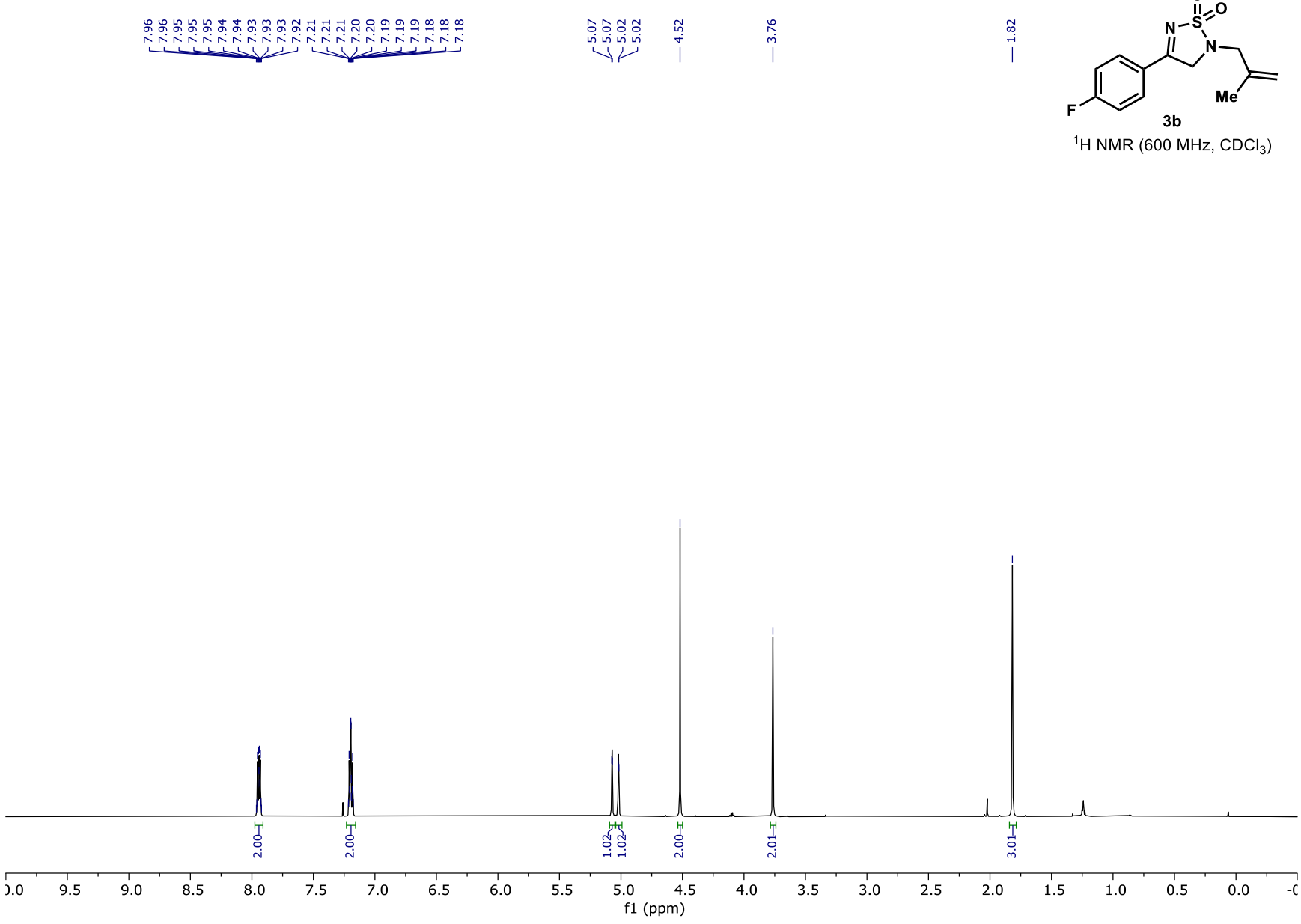

173.45
167.74
166.02
131.99
131.36
131.30
125.70
125.68
120.72
117.04
116.89
56.25
49.35
O
O
N
S
N
F
3a
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3a

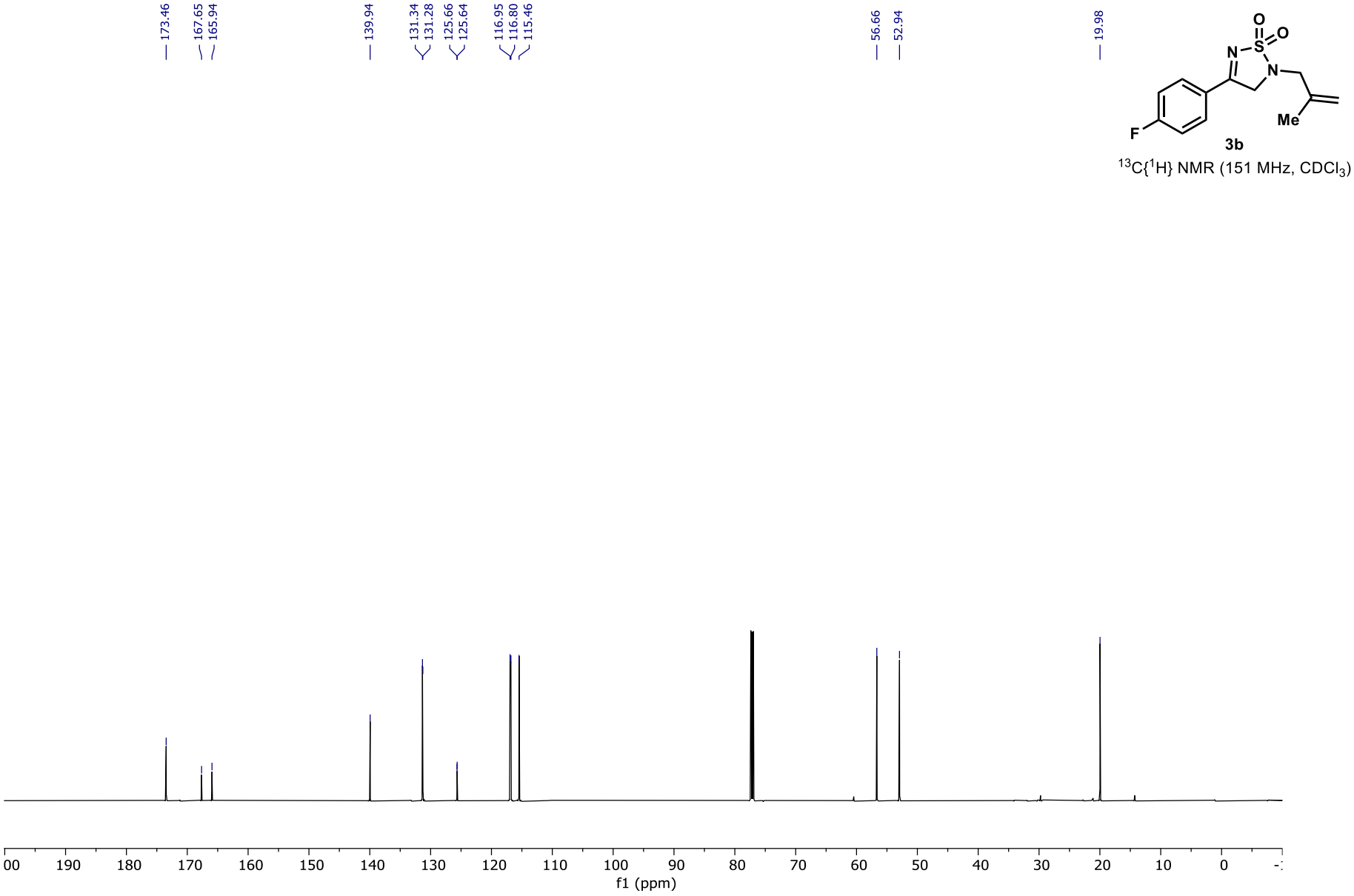
$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)





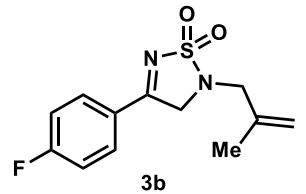
3b

^{1}H NMR (600 MHz, $CDCl_3$)



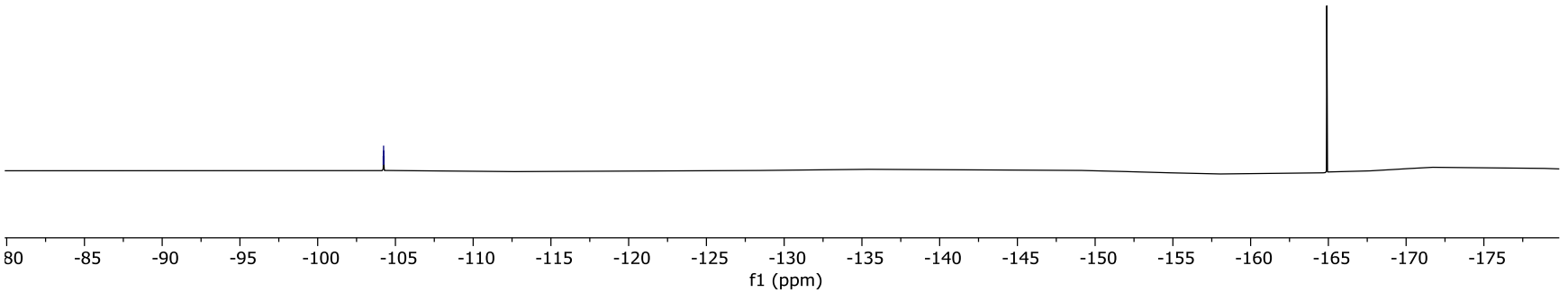
3b

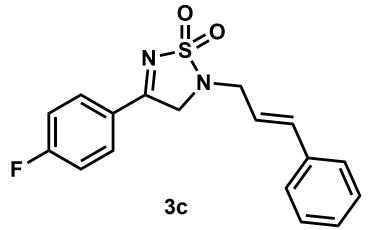
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



3b

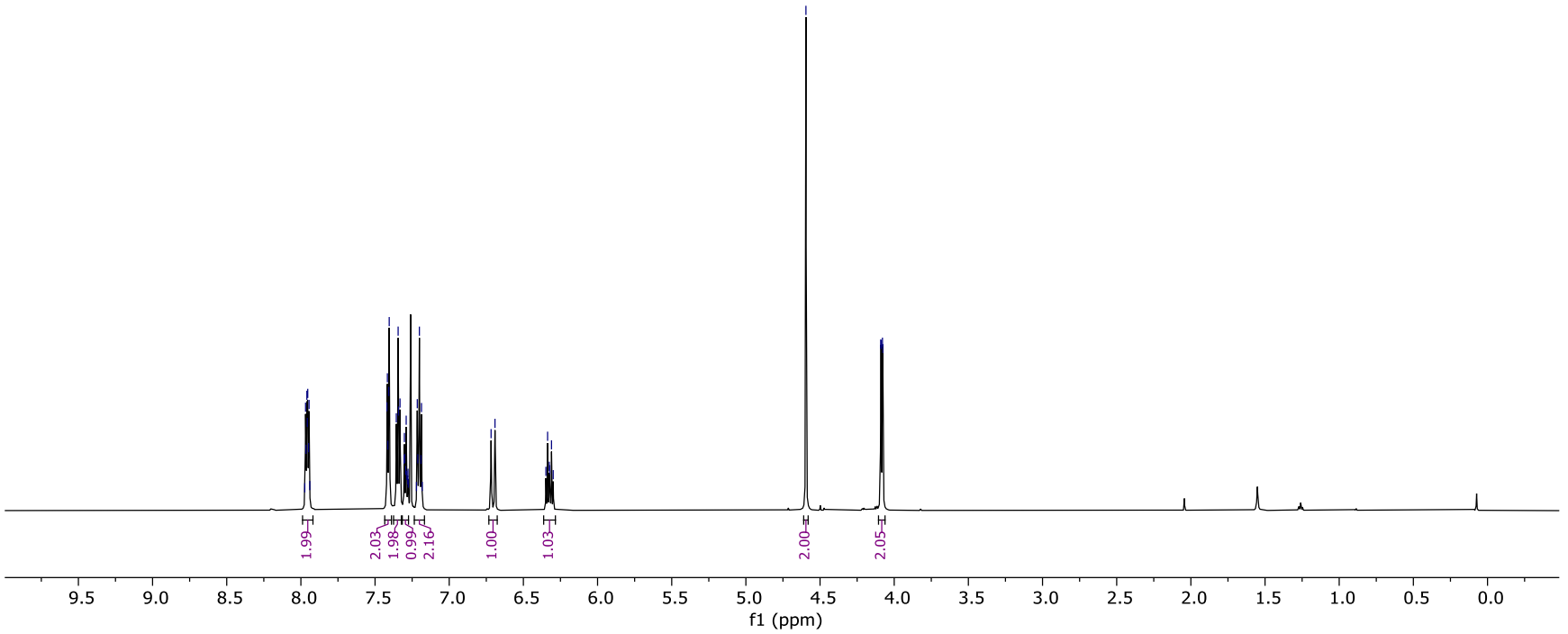
$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)

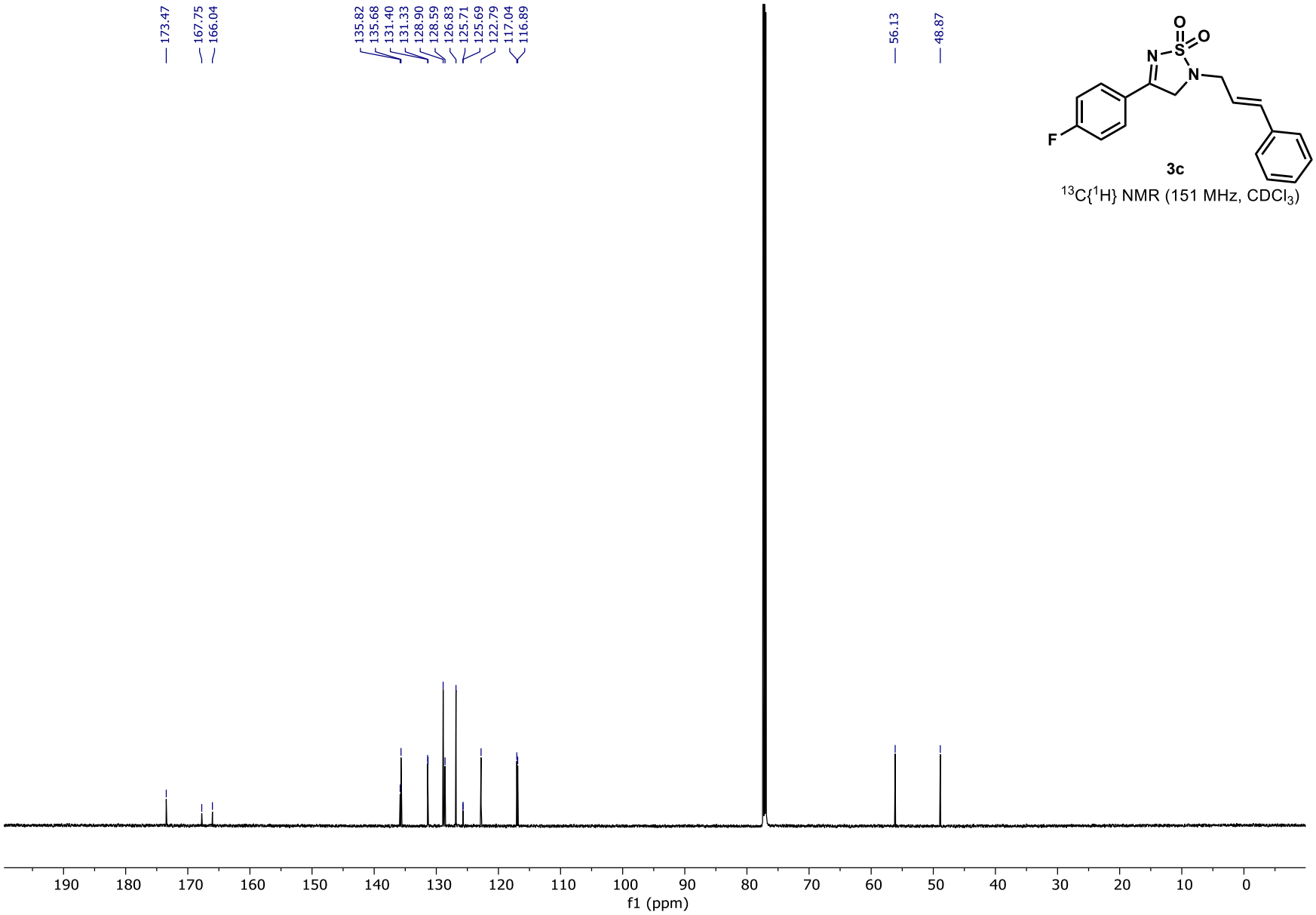


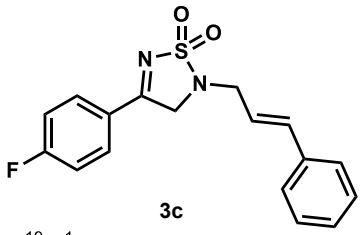


3c

^{1}H NMR (600 MHz, $CDCl_3$)

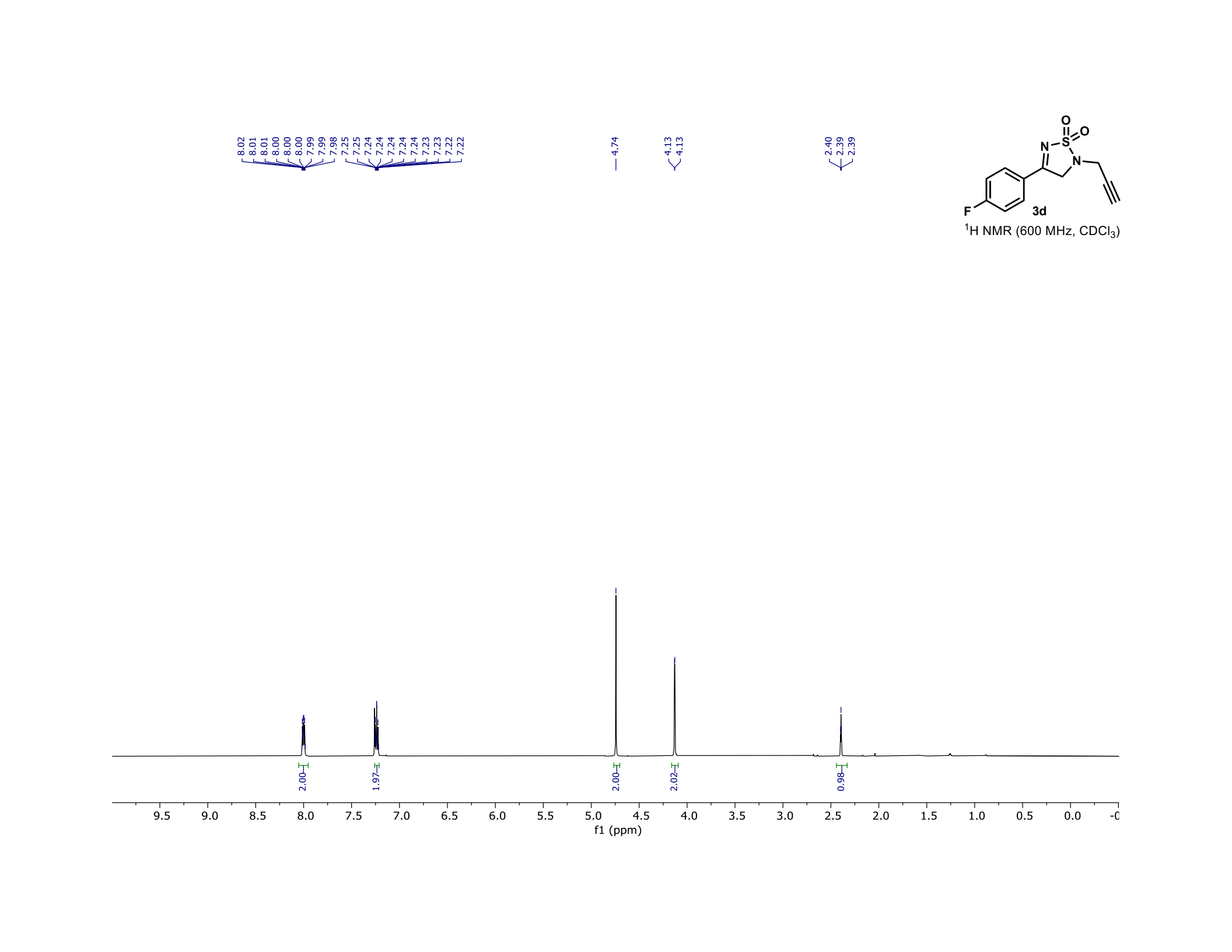



173.47
167.75
166.04
135.82
135.68
131.40
131.33
128.90
128.59
126.83
125.71
125.69
122.79
117.04
116.89
56.13
48.87
O
O
S
N
N
F
3c
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

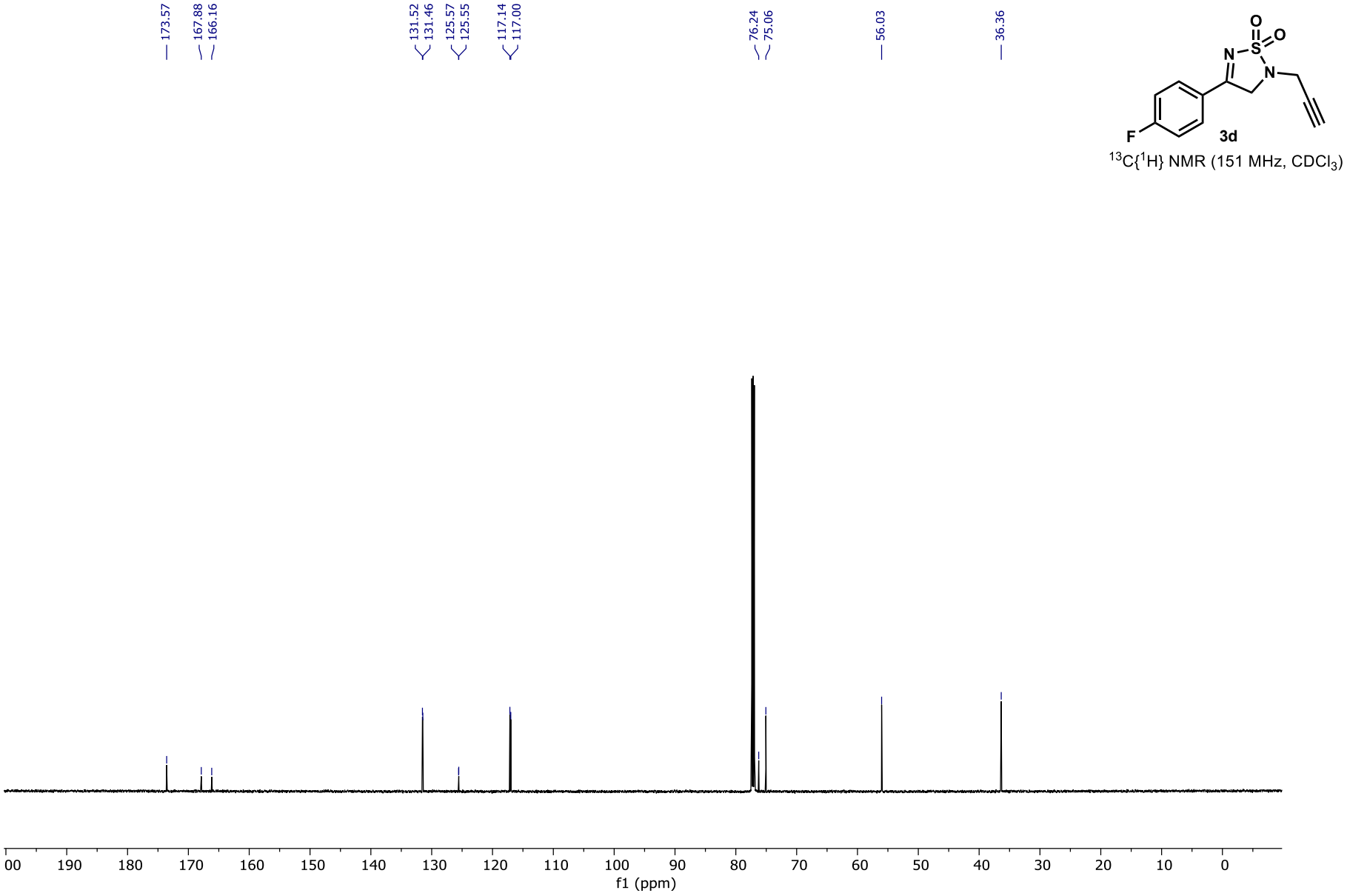


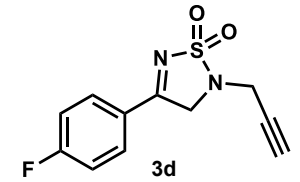
3c

$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



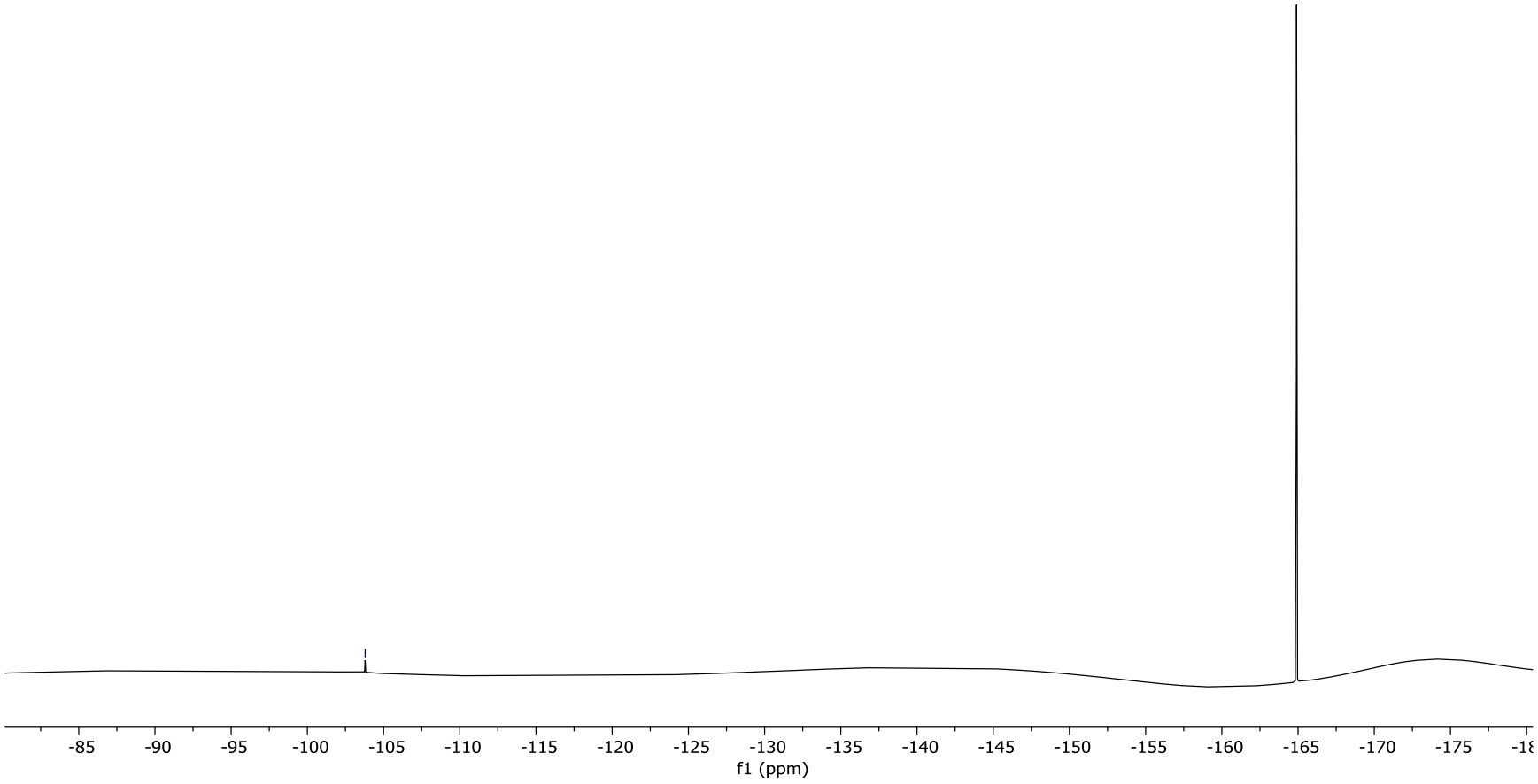
^{1}H NMR (600 MHz, $CDCl_3$)

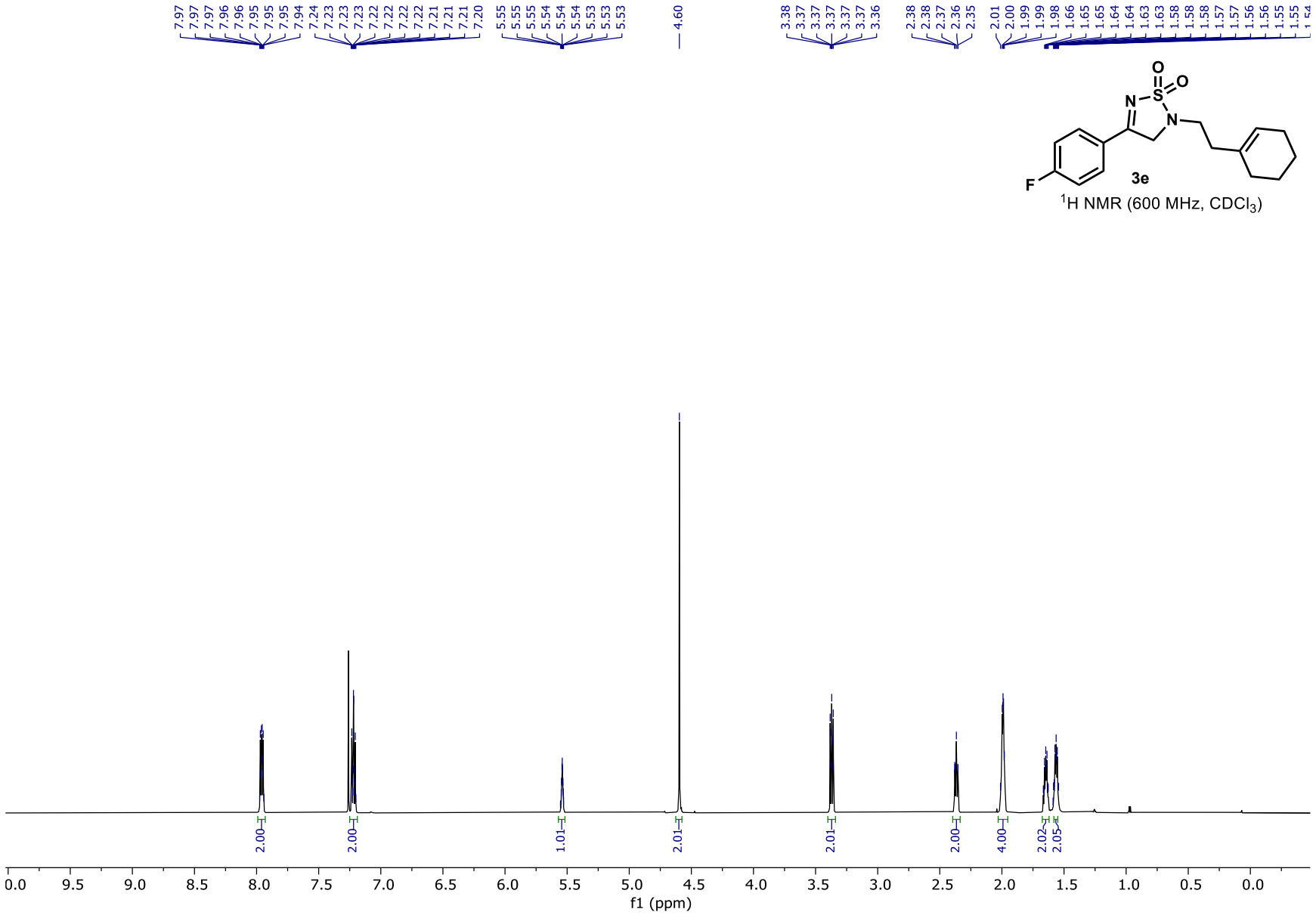

173.57
167.88
166.16
131.52
131.46
125.57
125.55
117.14
117.00
76.24
75.06
56.03
36.36
O
O
N
S
N
F
3d
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

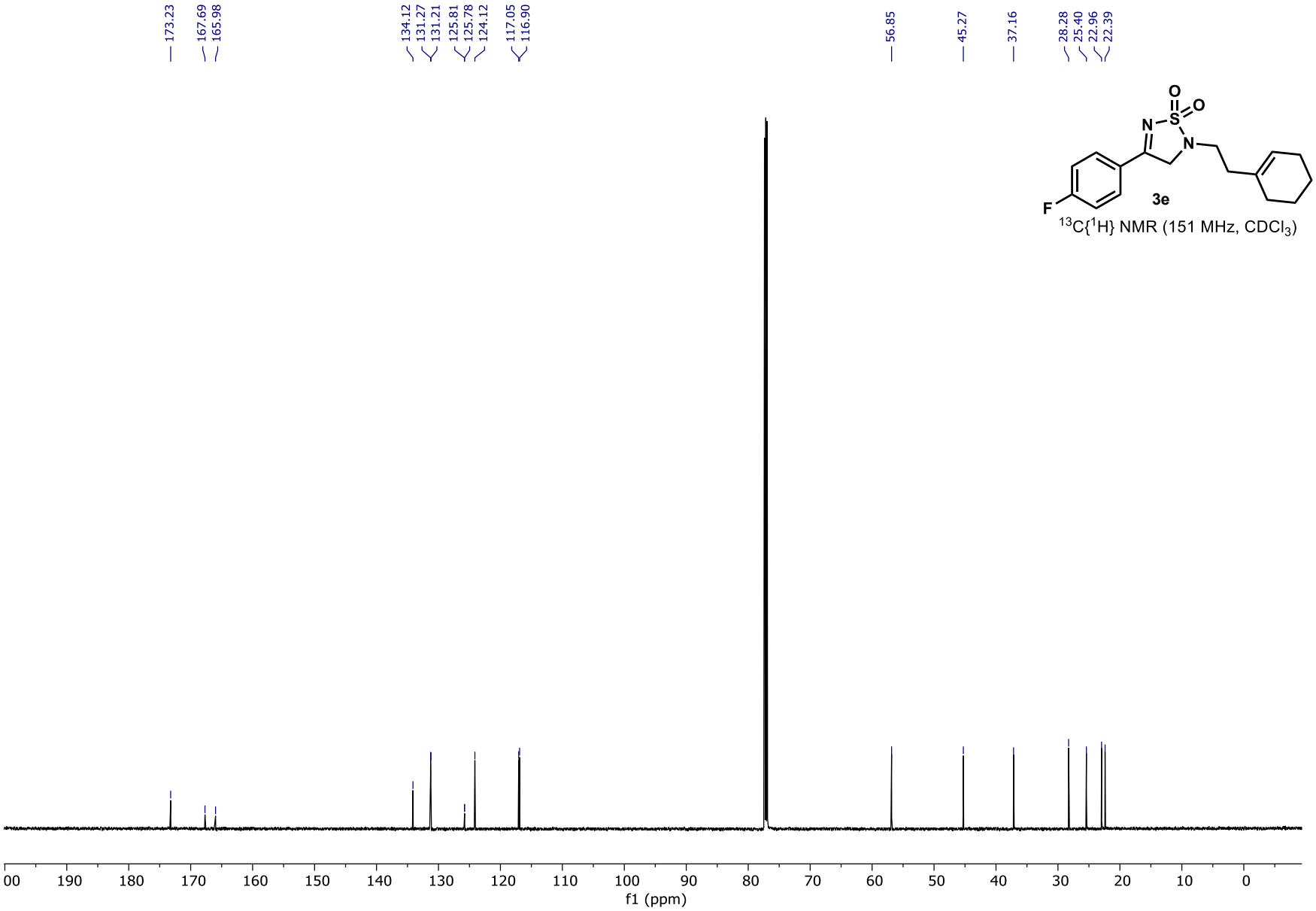


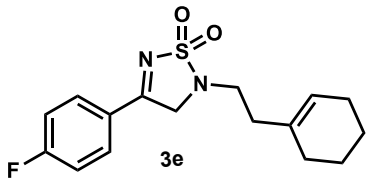
3d

$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)



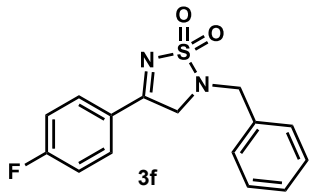

7.97 7.97 7.97 7.96 7.96 7.95 7.95 7.95 7.94
7.24 7.23 7.23 7.23 7.22 7.22 7.22 7.22 7.21 7.21 7.20
5.55 5.55 5.55 5.54 5.54 5.54 5.53 5.53 5.53
4.60
3.38 3.37 3.37 3.37 3.37 3.37 3.36
2.38 2.38 2.37 2.36 2.35
2.01 2.00 1.99 1.99 1.98 1.66 1.65 1.65 1.64 1.64 1.63 1.63 1.58 1.58 1.57 1.57 1.56 1.56 1.55 1.55
O
O
N
S
N
F
3e
^{1}H NMR (600 MHz, $CDCl_3$)
2.00
2.00
1.01
2.01
2.01
2.00
4.00
2.02
2.05
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.23
167.69
165.98
134.12
131.27
131.21
125.81
125.78
124.12
117.05
116.90
56.85
45.27
37.16
28.28
25.40
22.96
22.39
O
O
N
S
N
F
3e
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
f1 (ppm)



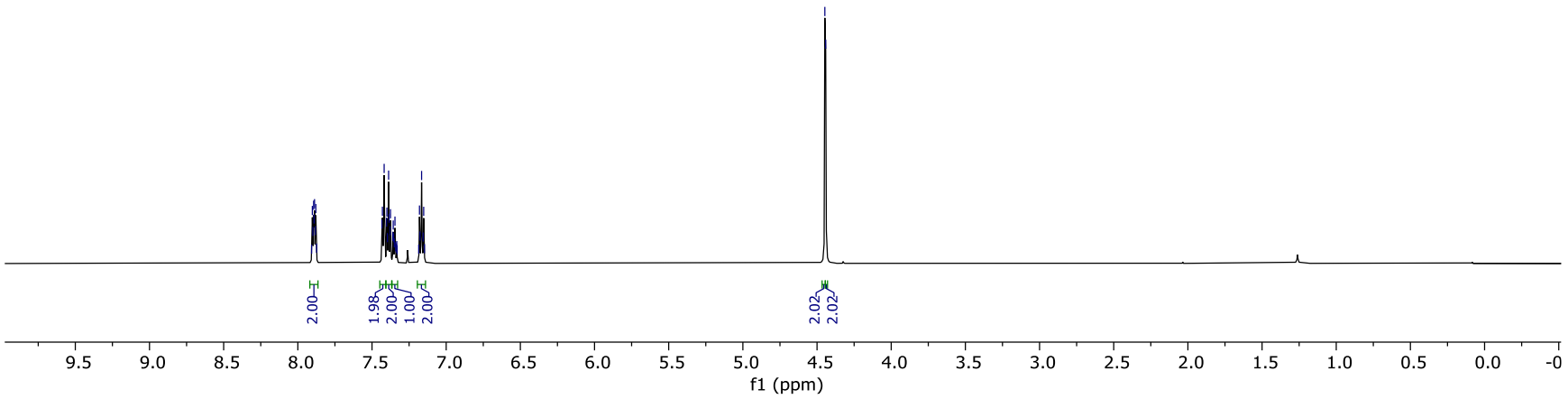
3e

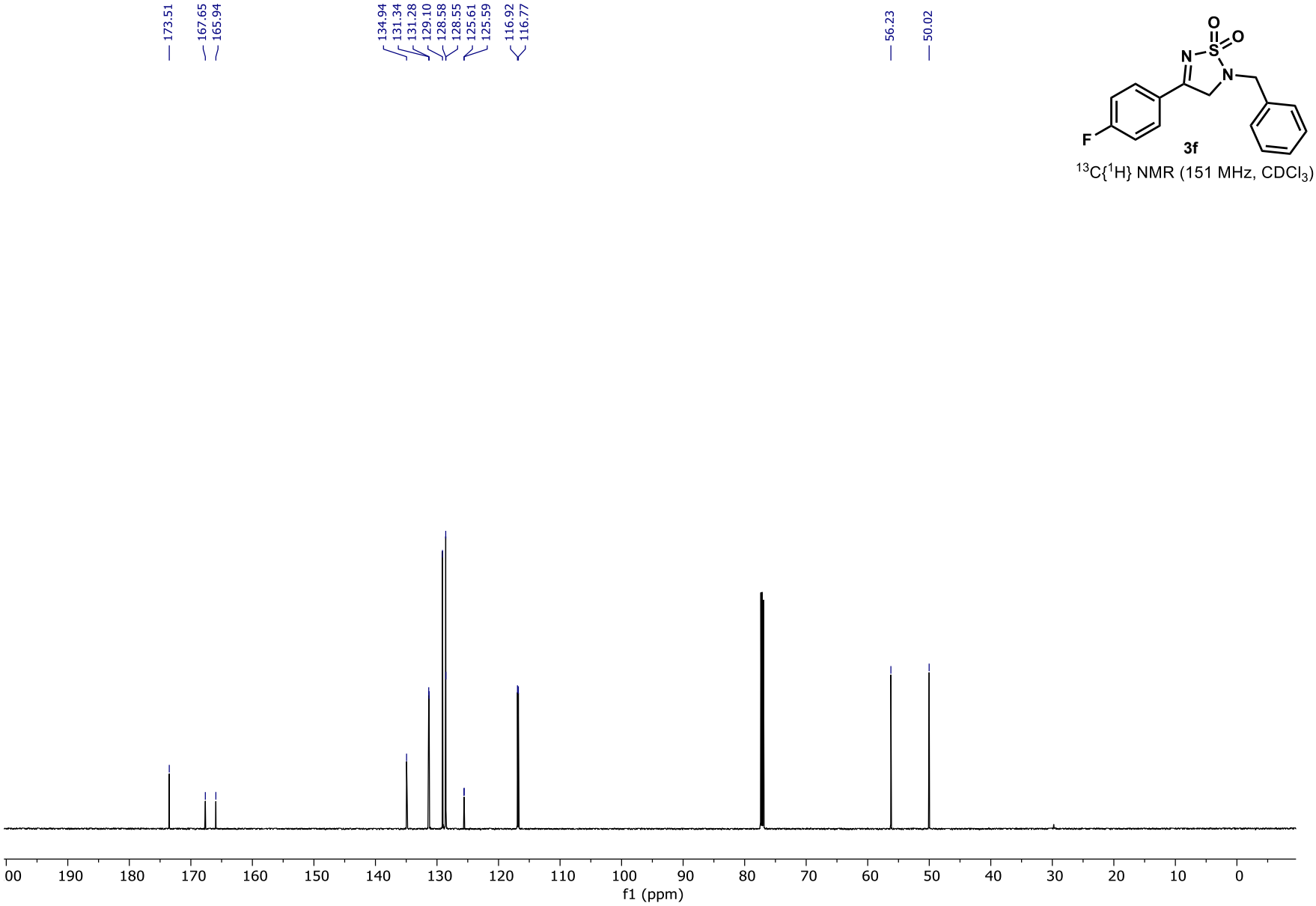
$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)

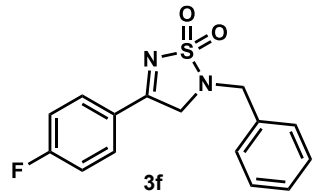


3f

^{1}H NMR (600 MHz, $CDCl_3$)

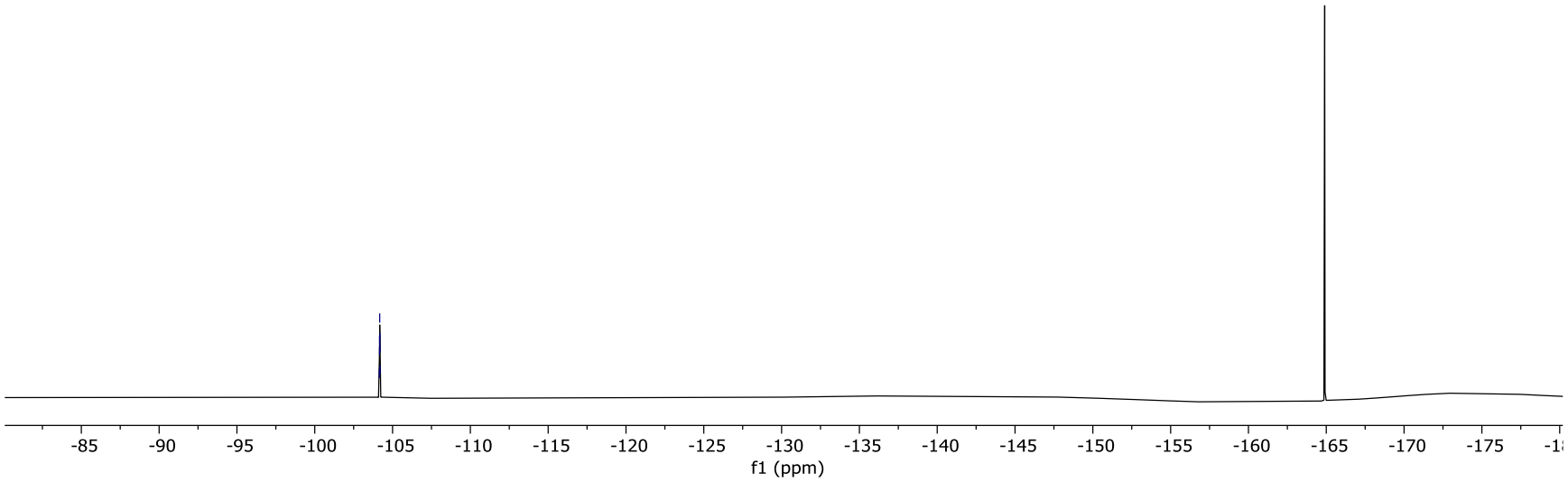


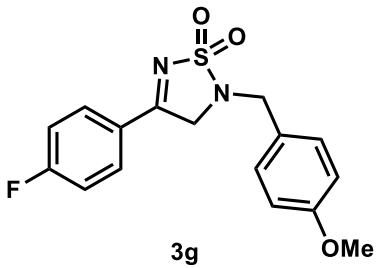

173.51
167.65
165.94
134.94
131.34
131.28
129.10
128.58
128.55
125.61
125.59
116.92
116.77
56.23
50.02
O
O
N
S
N
F
3f
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3f

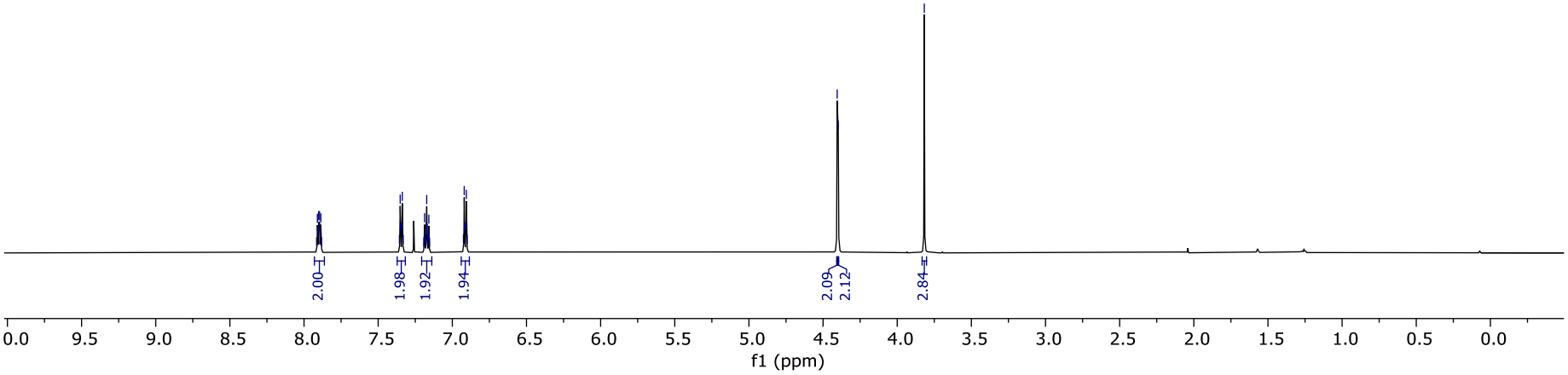
$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)

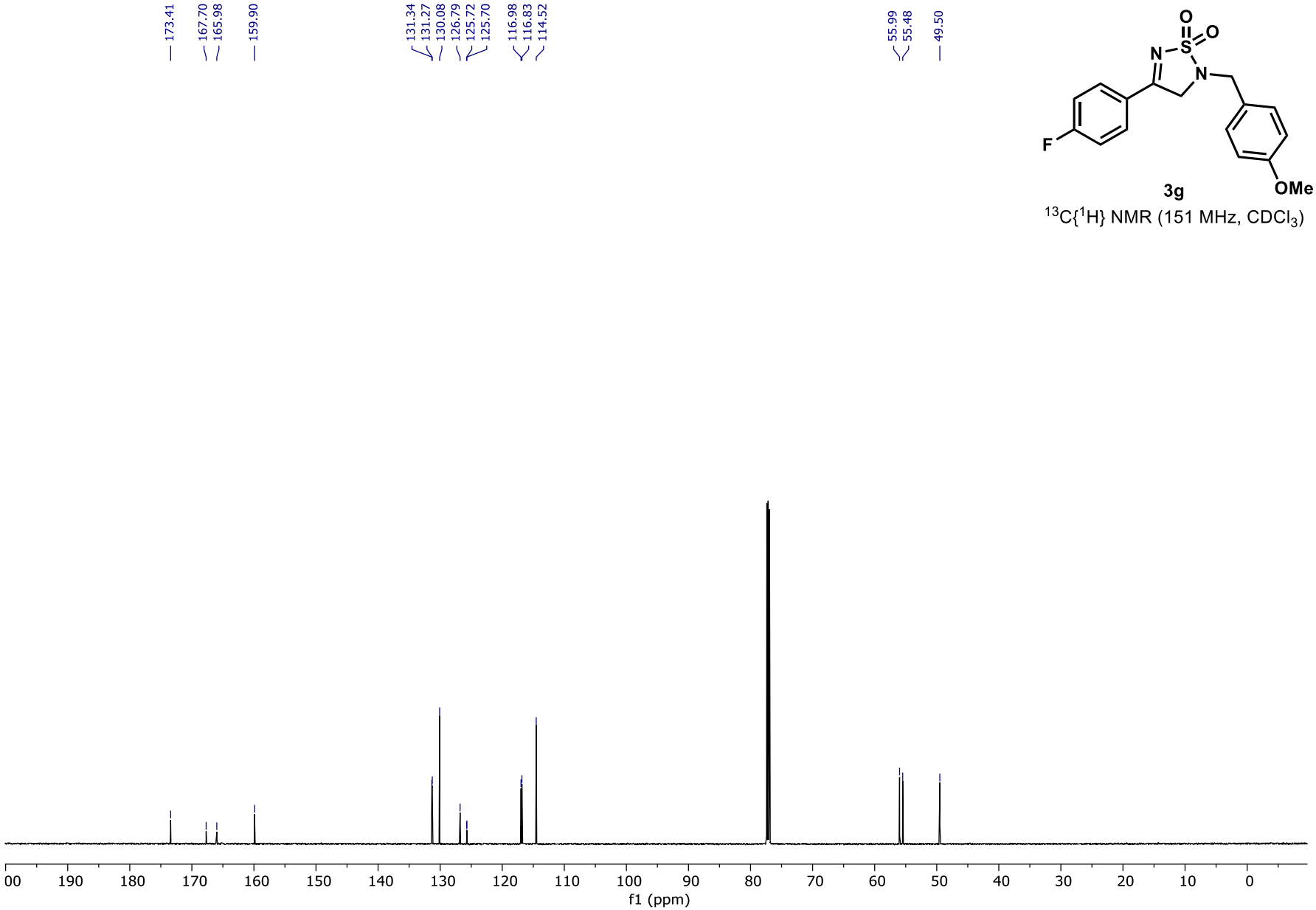


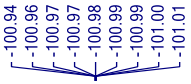


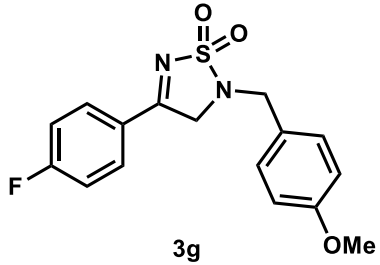
3g

^{1}H NMR (600 MHz, $CDCl_3$)



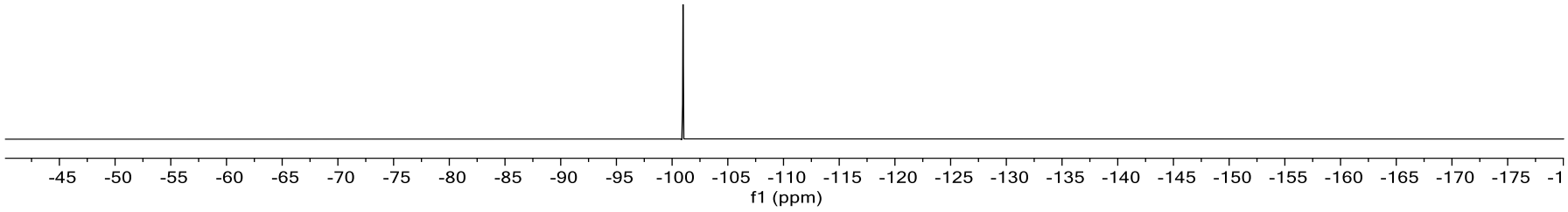

173.41
167.70
165.98
159.90
131.34
131.27
130.08
126.79
125.72
125.70
116.98
116.83
114.52
55.99
55.48
49.50
O
O
N
S
N
F
OMe
3g
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

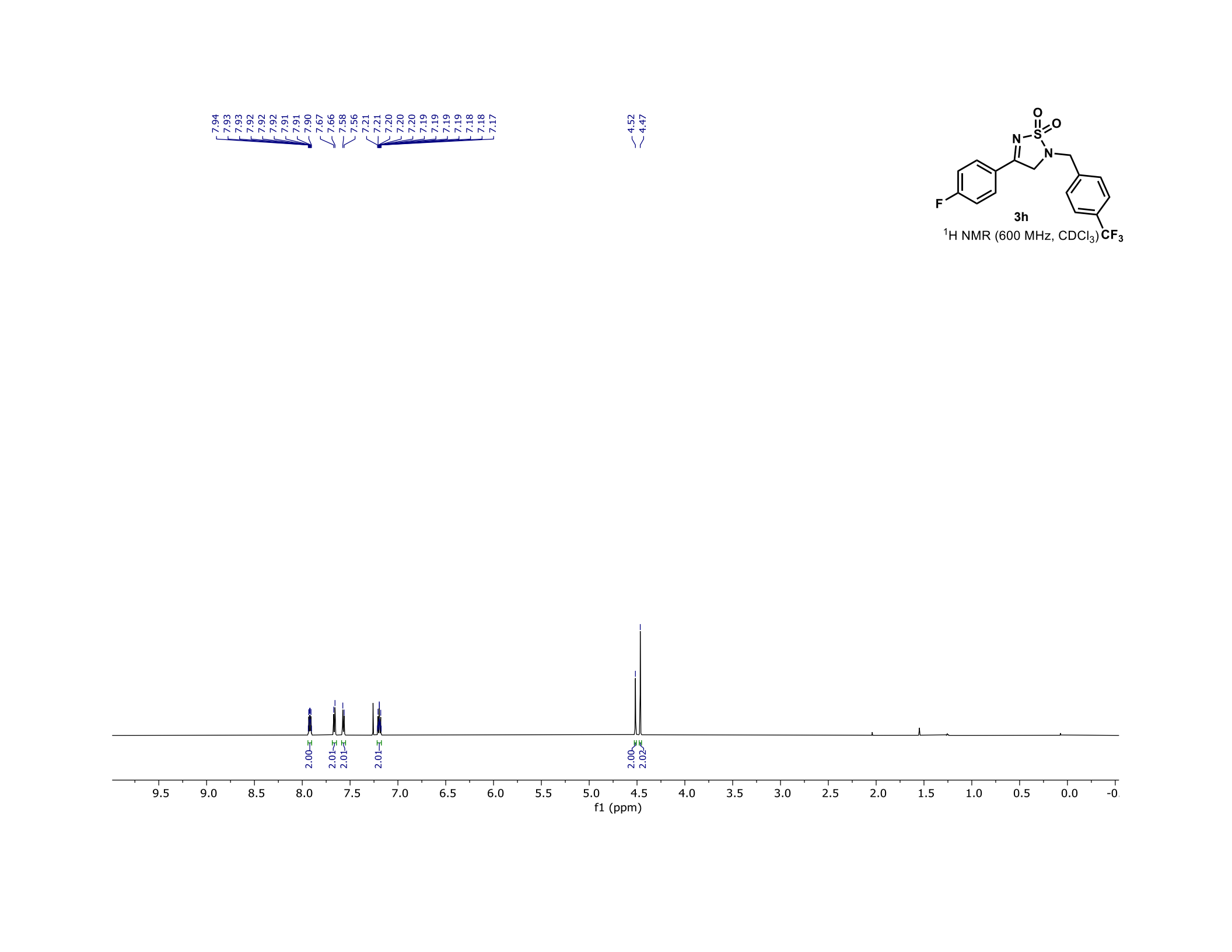


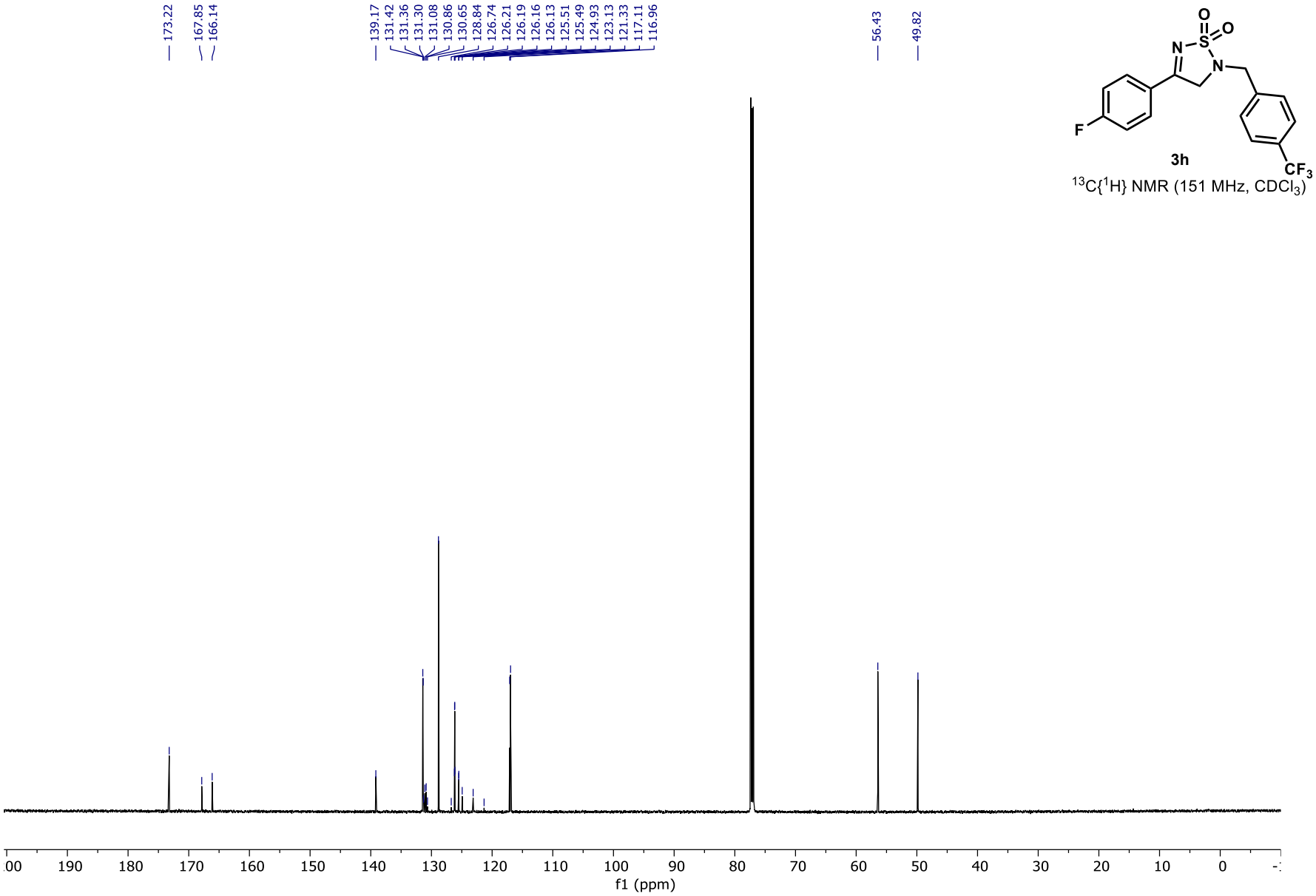


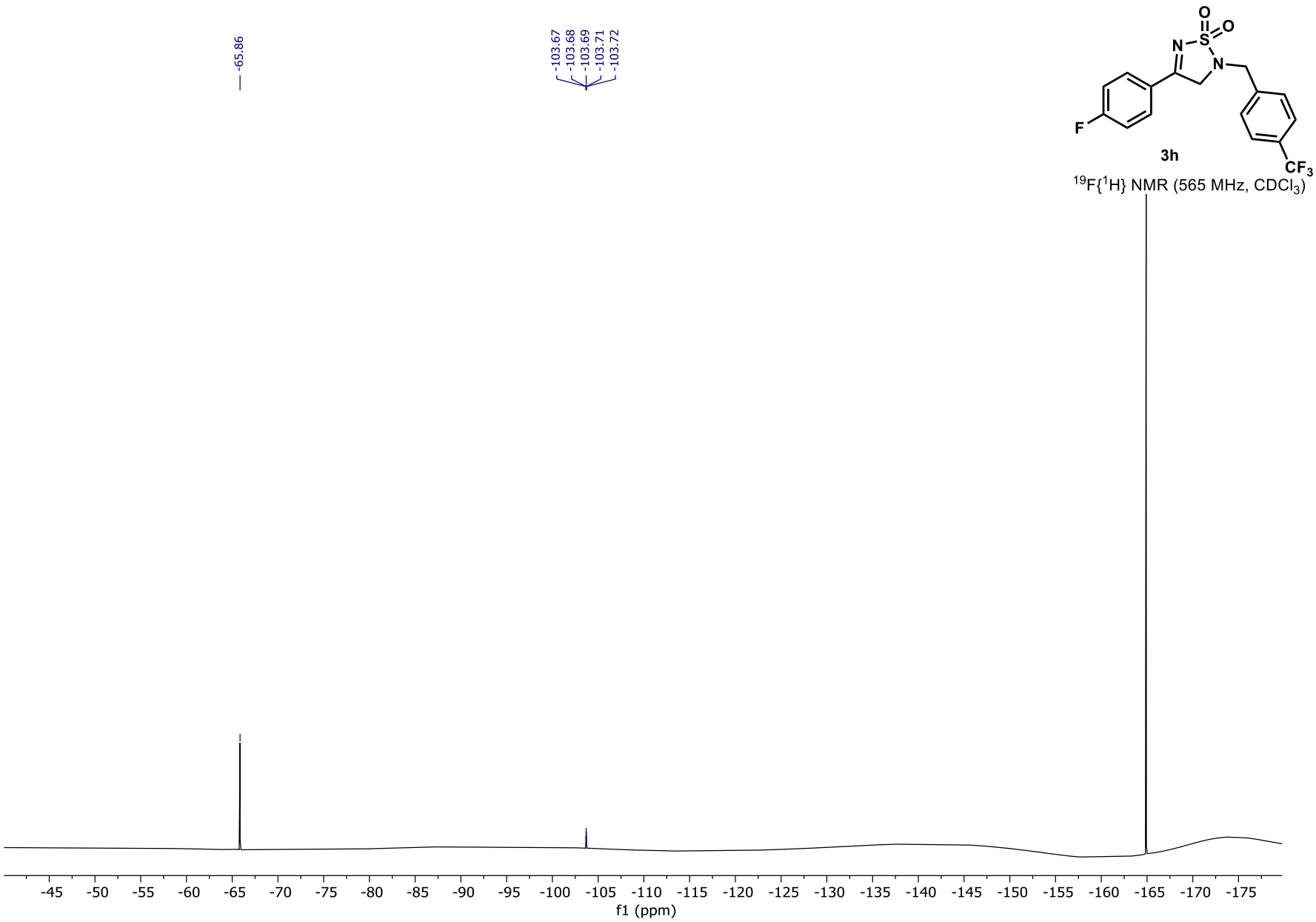
3g

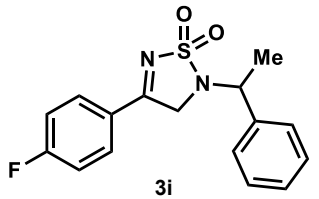
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)




7.94
7.93
7.93
7.92
7.92
7.92
7.91
7.91
7.90
7.67
7.66
7.58
7.56
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.19
7.19
7.18
7.18
7.17
4.52
4.47
O
O
N
S
N
F
CF3
3h
1H NMR (600 MHz, CDCl3)
2.00
2.01
2.01
2.01
2.00
2.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

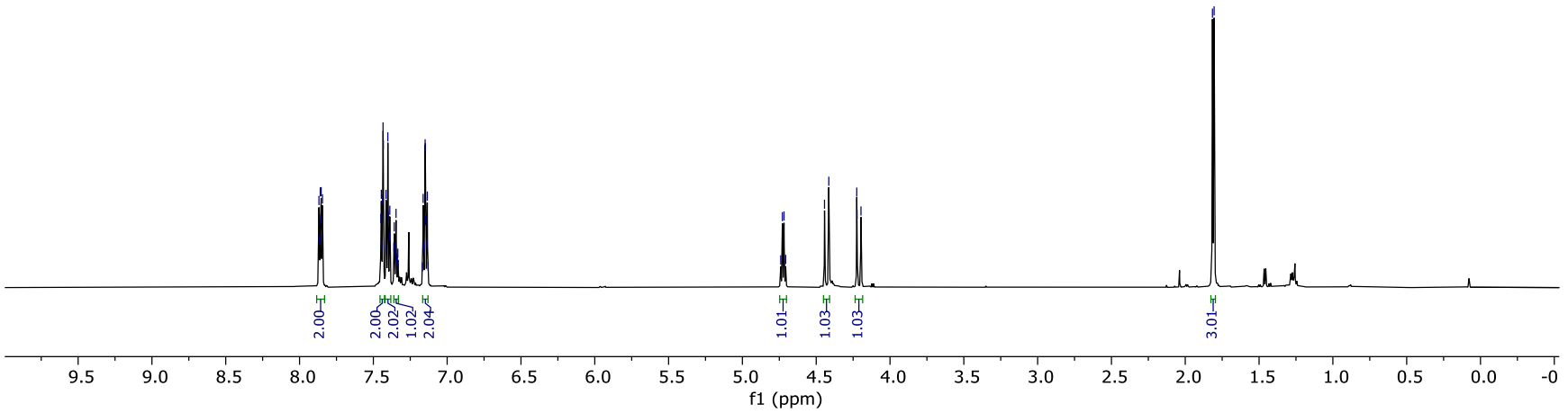

173.22
167.85
166.14
139.17
131.42
131.36
131.30
131.08
130.86
130.65
128.84
126.74
126.21
126.19
126.16
126.13
125.51
125.49
124.93
123.13
121.33
117.11
116.96
56.43
49.82
O
O
N
S
N
F
CF3
3h
13C{1H} NMR (151 MHz, CDCl3)
f1 (ppm)

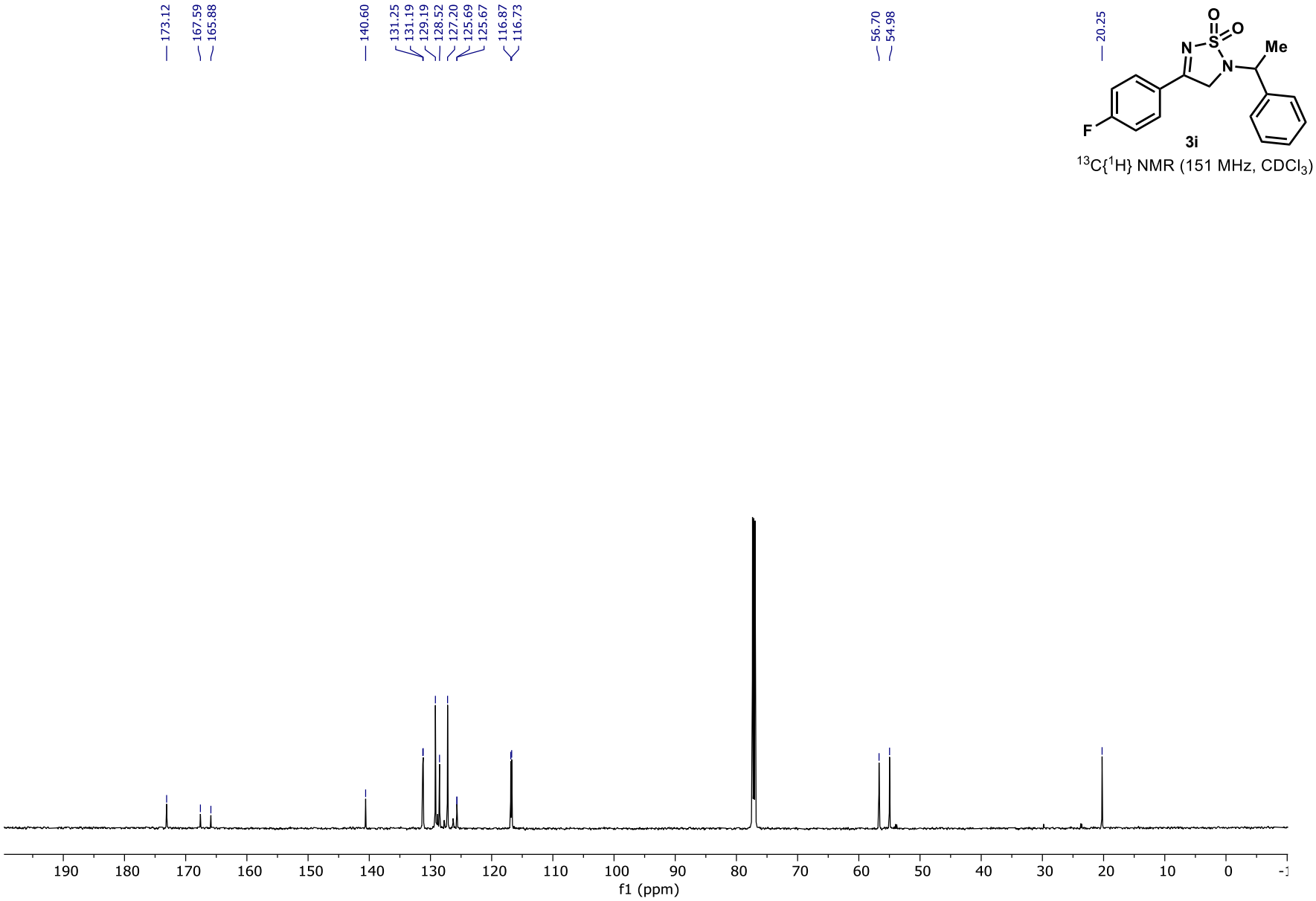

-65.86
-103.67
-103.68
-103.69
-103.71
-103.72
O
O
N
S
N
F
CF3
3h
19F{1H} NMR (565 MHz, CDCl3)
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175
f1 (ppm)



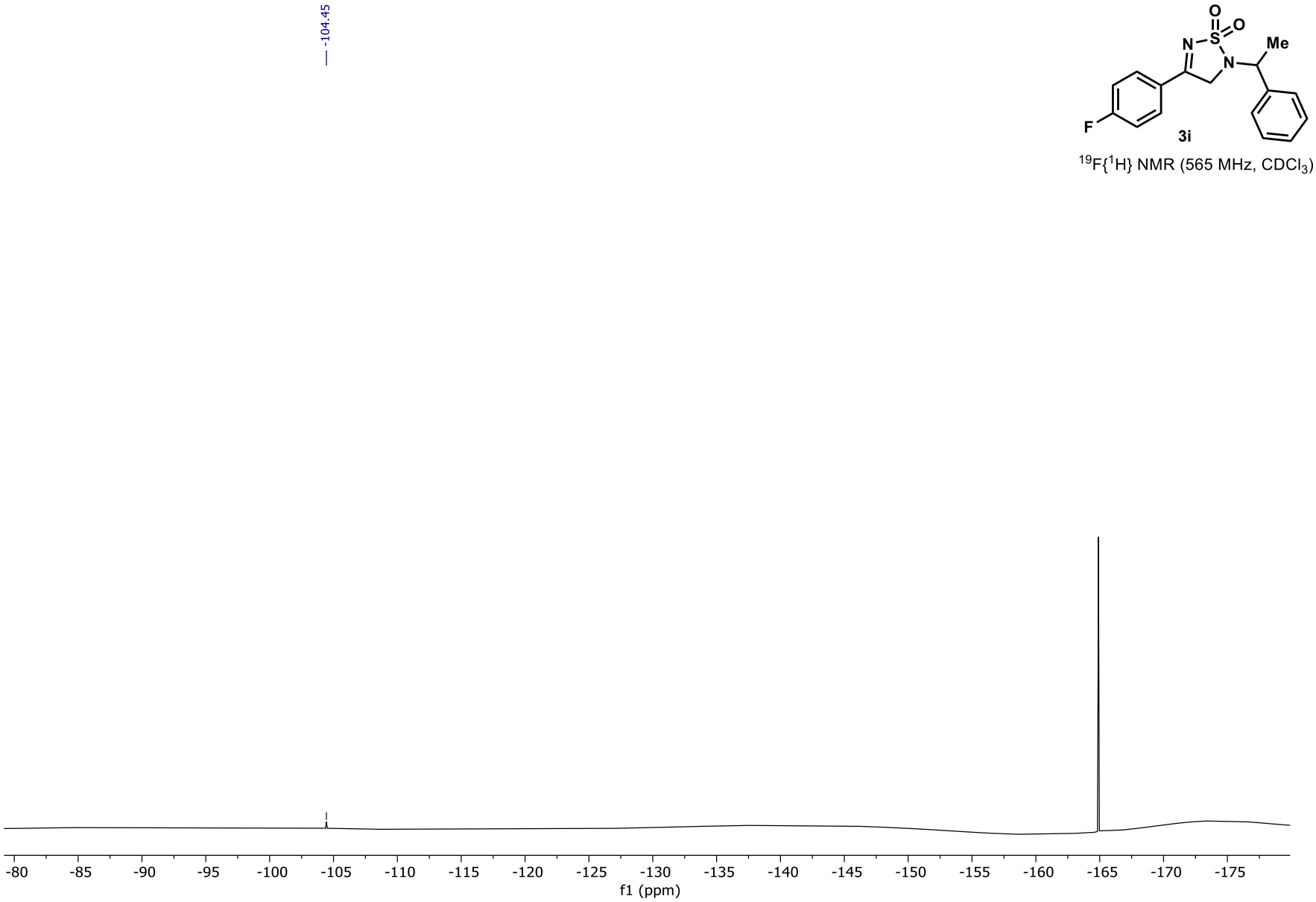
3i

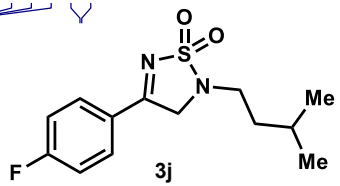
^{1}H NMR (600 MHz, $CDCl_3$)





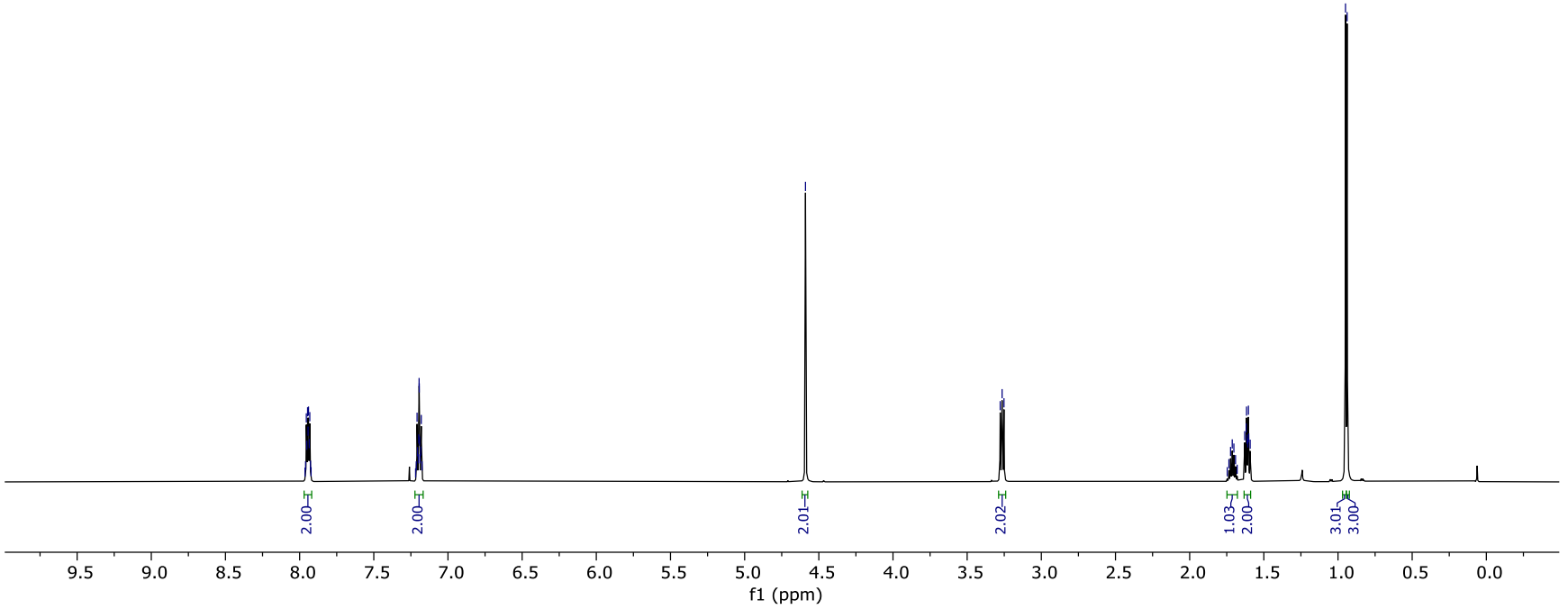
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

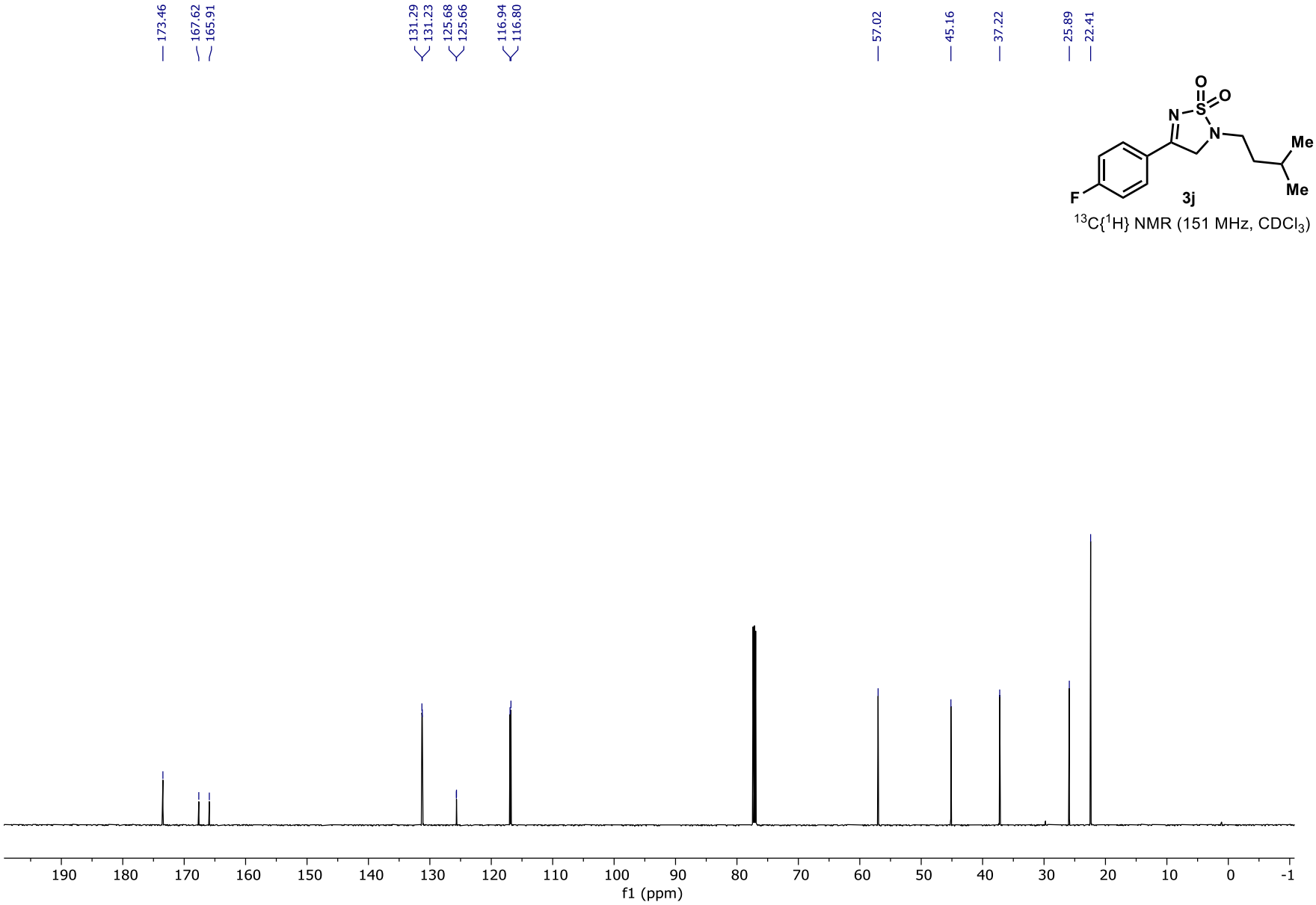

-104.45
O
O
N
S
Me
N
F
3i
$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
f1 (ppm)

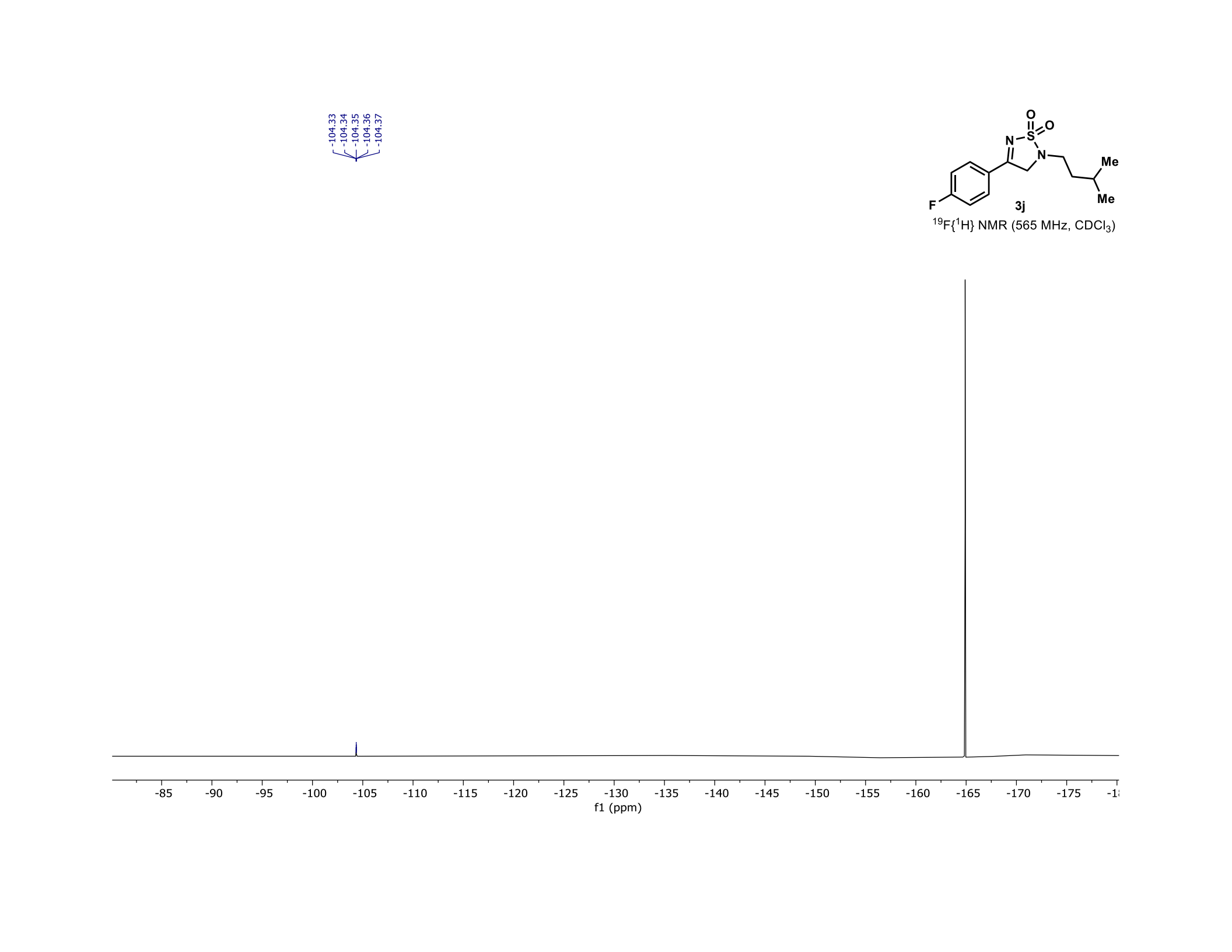


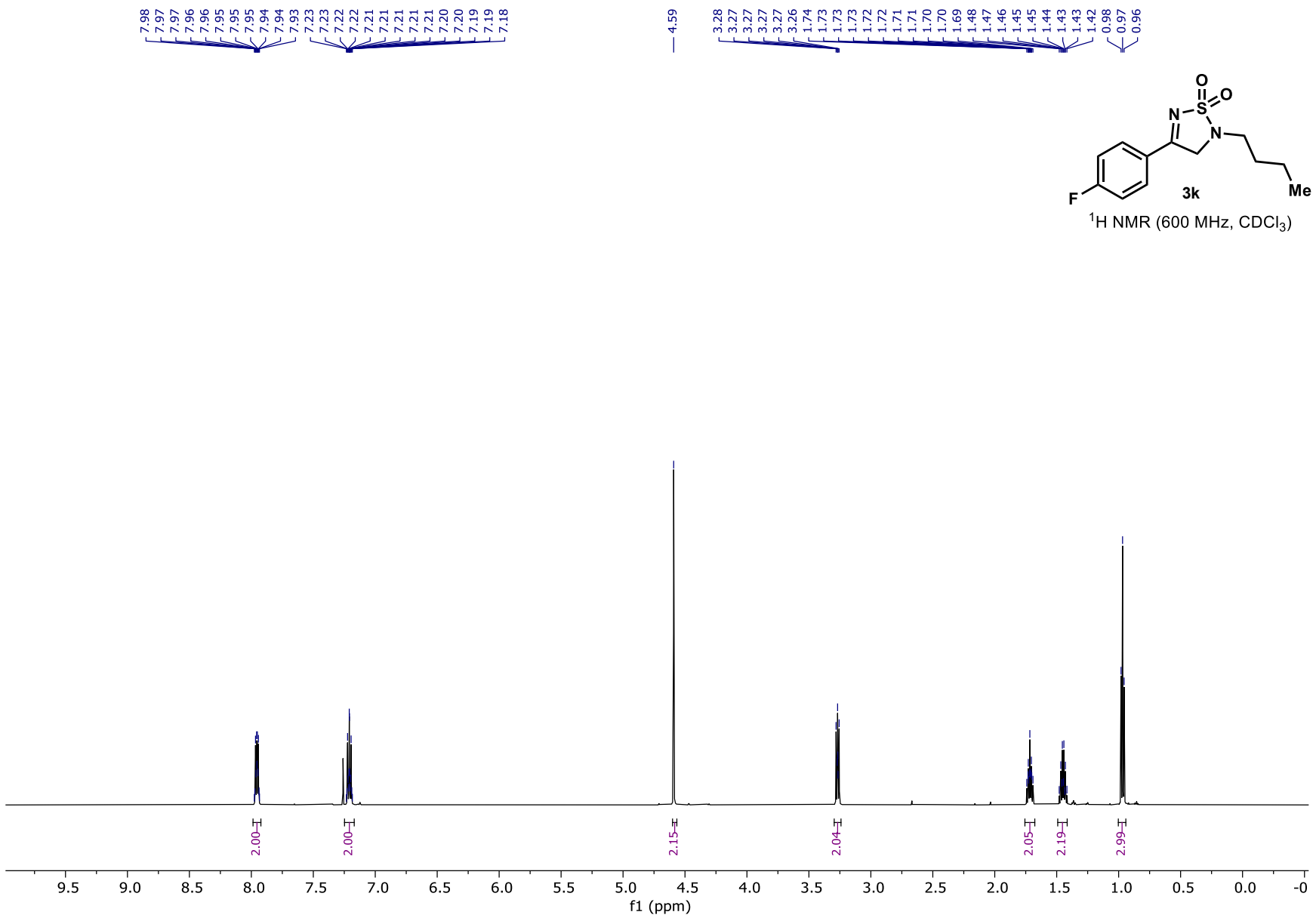
3j

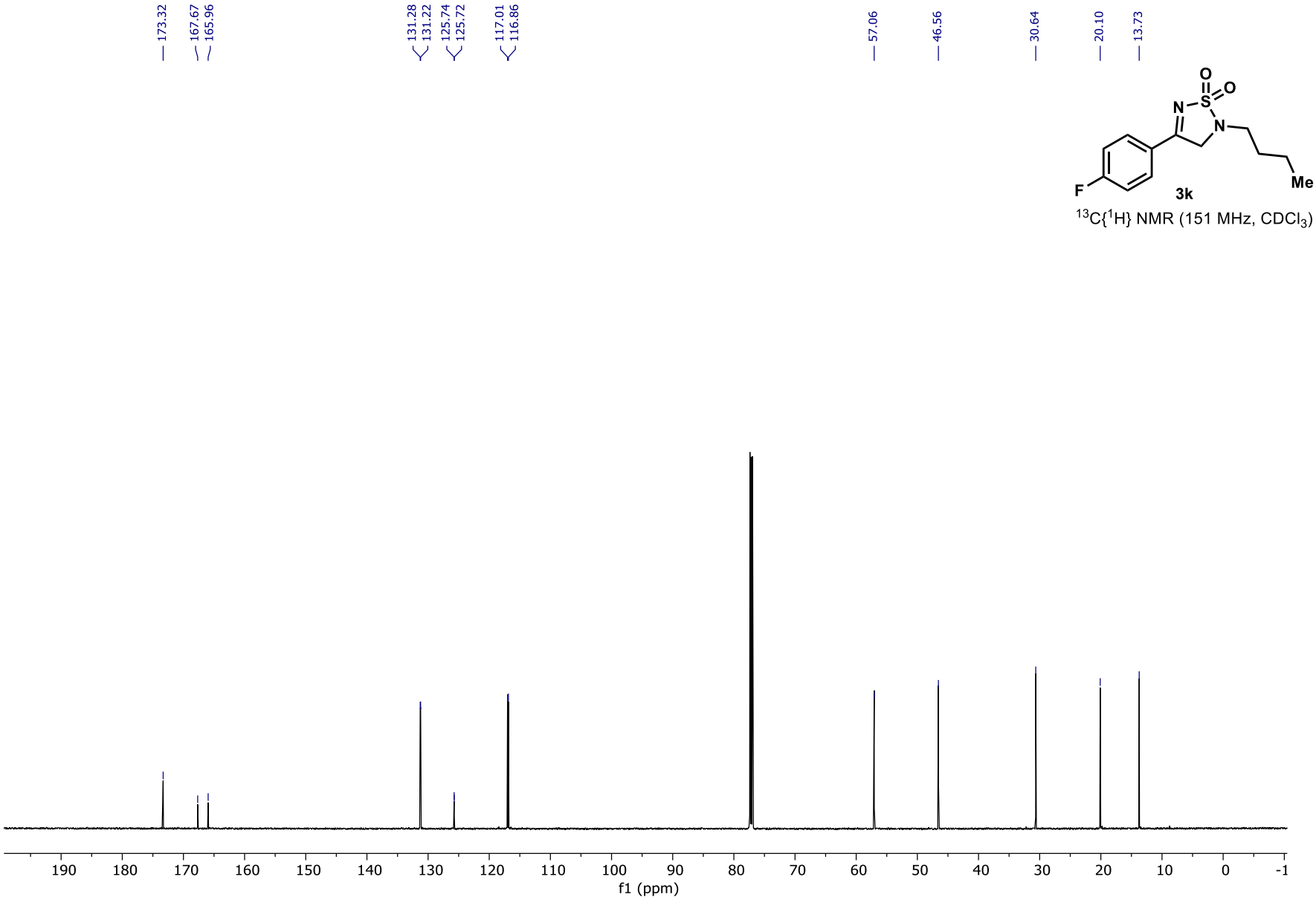
^{1}H NMR (600 MHz, $CDCl_3$)

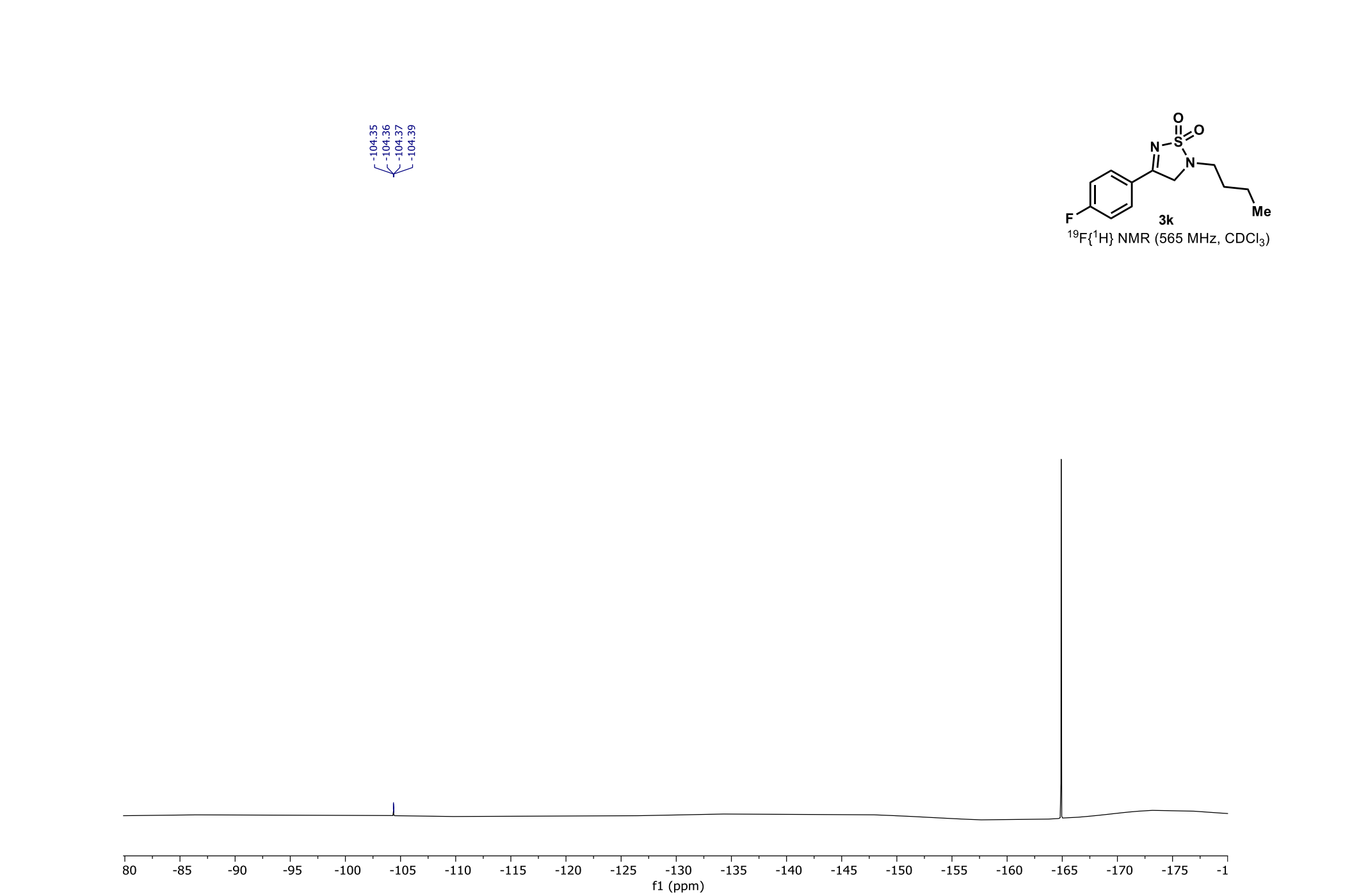


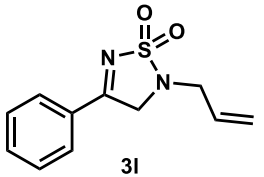

173.46
167.62
165.91
131.29
131.23
125.68
125.66
116.94
116.80
57.02
45.16
37.22
25.89
22.41
O
O
N
S
N
Me
Me
F
3j
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


-104.33
-104.34
-104.35
-104.36
-104.37
O
O
N
S
N
Me
Me
F
3j
$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
f1 (ppm)


7.98
7.97
7.97
7.96
7.96
7.95
7.95
7.95
7.94
7.94
7.93
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.21
7.20
7.20
7.19
7.19
7.18
4.59
3.28
3.27
3.27
3.27
3.27
3.26
1.74
1.73
1.73
1.73
1.72
1.72
1.71
1.71
1.70
1.70
1.69
1.48
1.47
1.46
1.45
1.45
1.44
1.43
1.43
1.42
0.98
0.97
0.96
O
O
N
S
N
F
Me
3k
^{1}H NMR (600 MHz, $CDCl_3$)
2.00
2.00
2.15
2.04
2.05
2.19
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

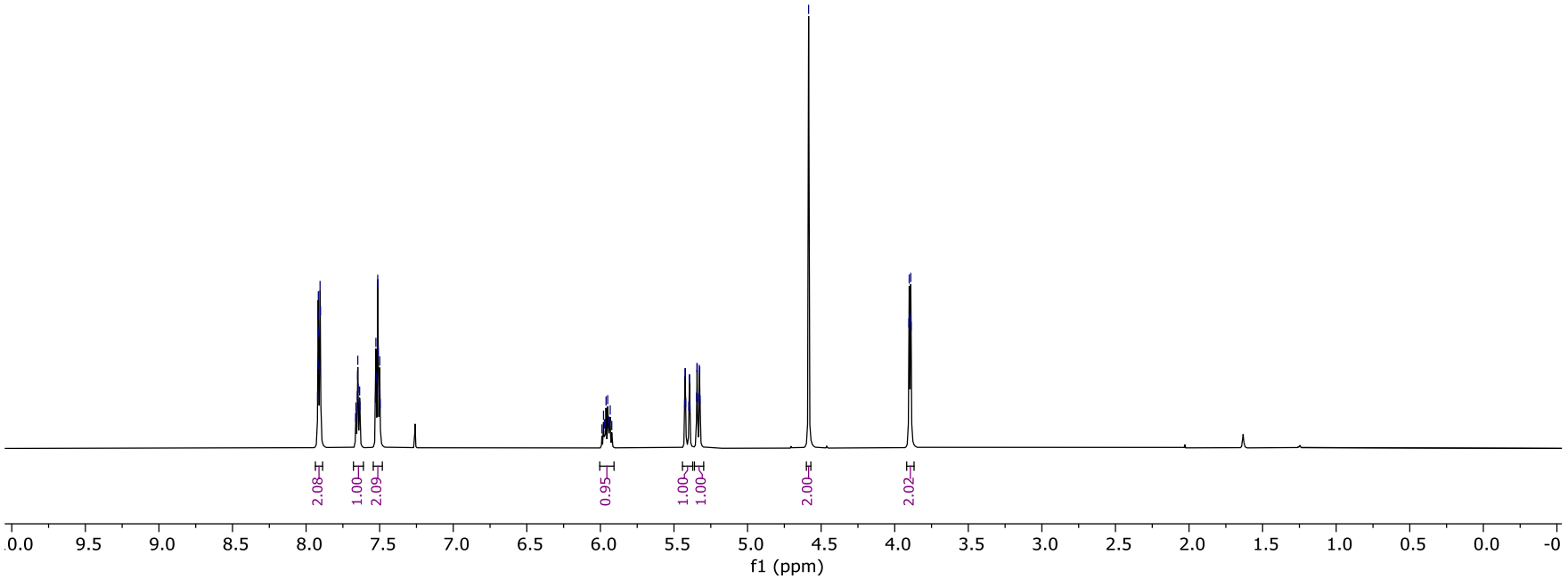

173.32
167.67
165.96
131.28
131.22
125.74
125.72
117.01
116.86
57.06
46.56
30.64
20.10
13.73
O
O
N
S
N
F
Me
3k
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

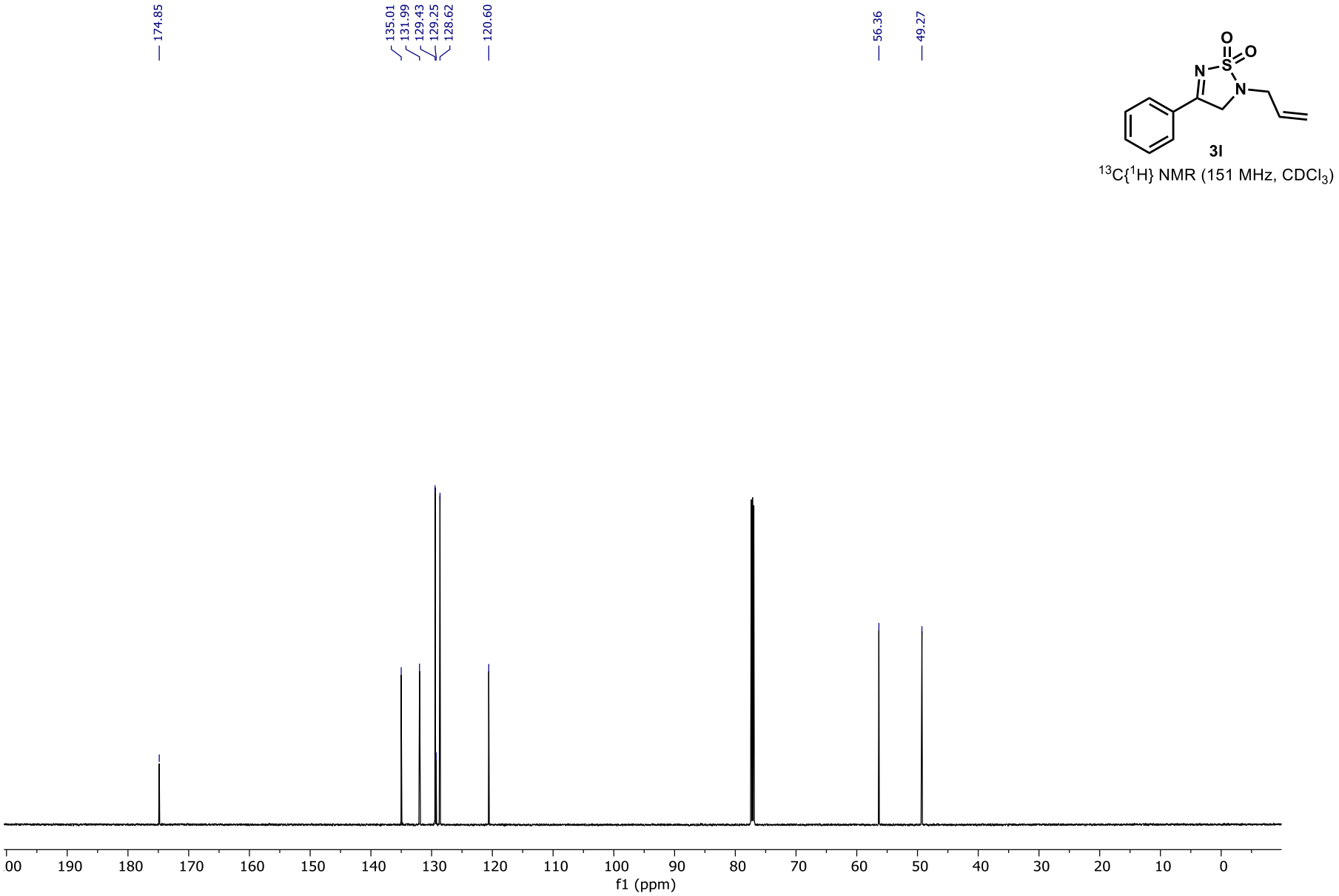

-104.35
-104.36
-104.37
-104.39
O
O
N
S
N
F
Me
3k
$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)
80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-1
f1 (ppm)



3l

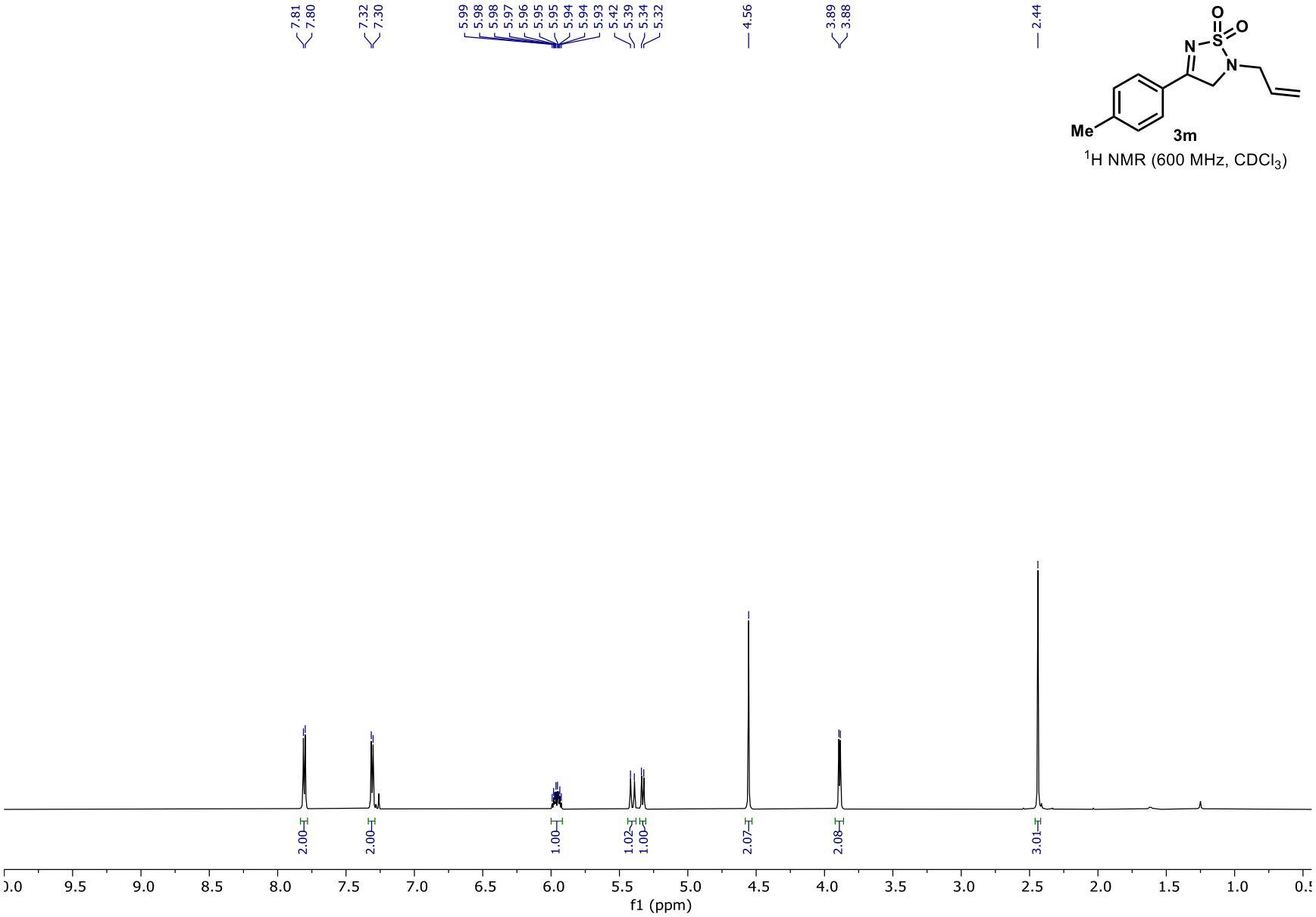
^{1}H NMR (600 MHz, $CDCl_3$)



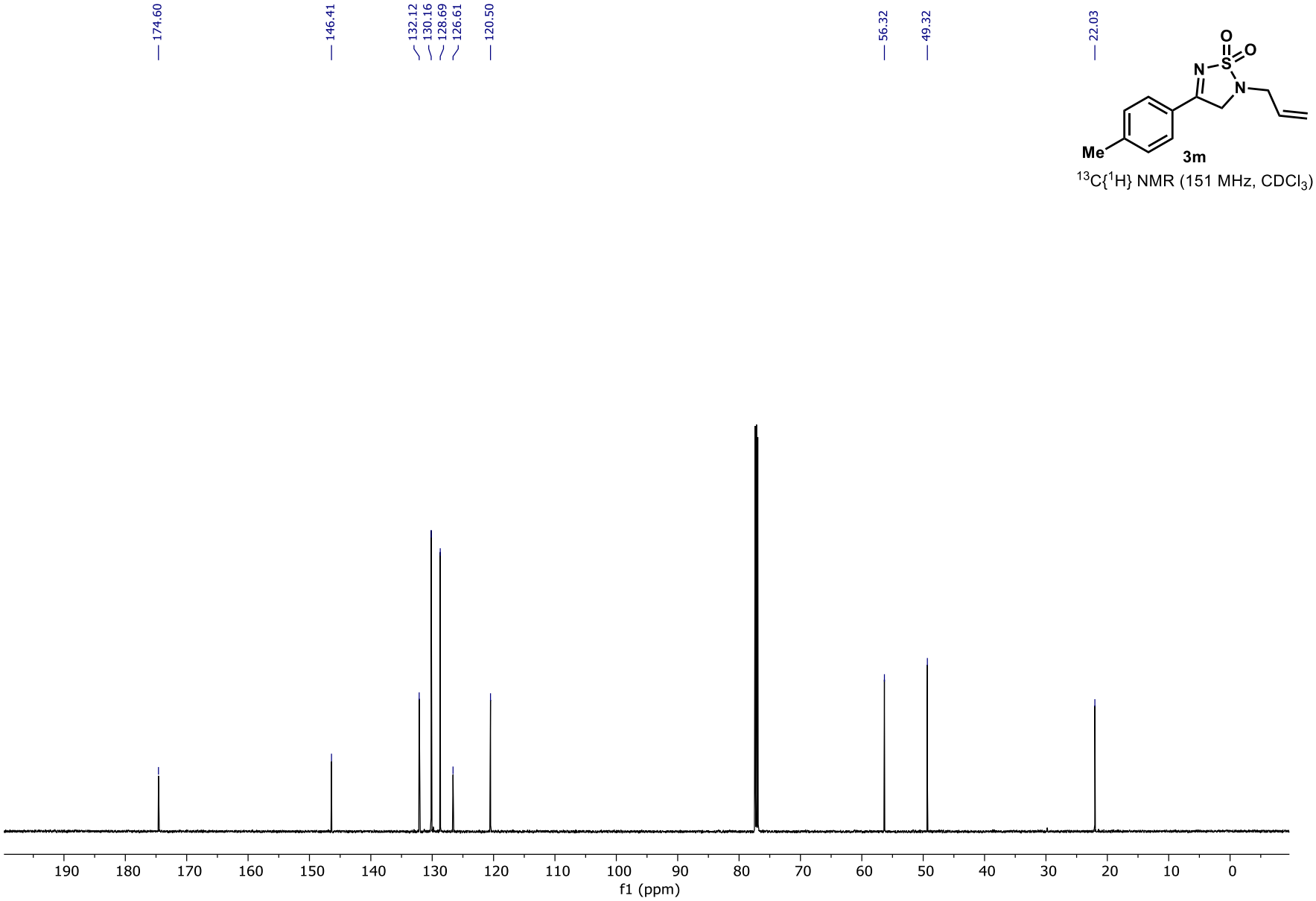


3l

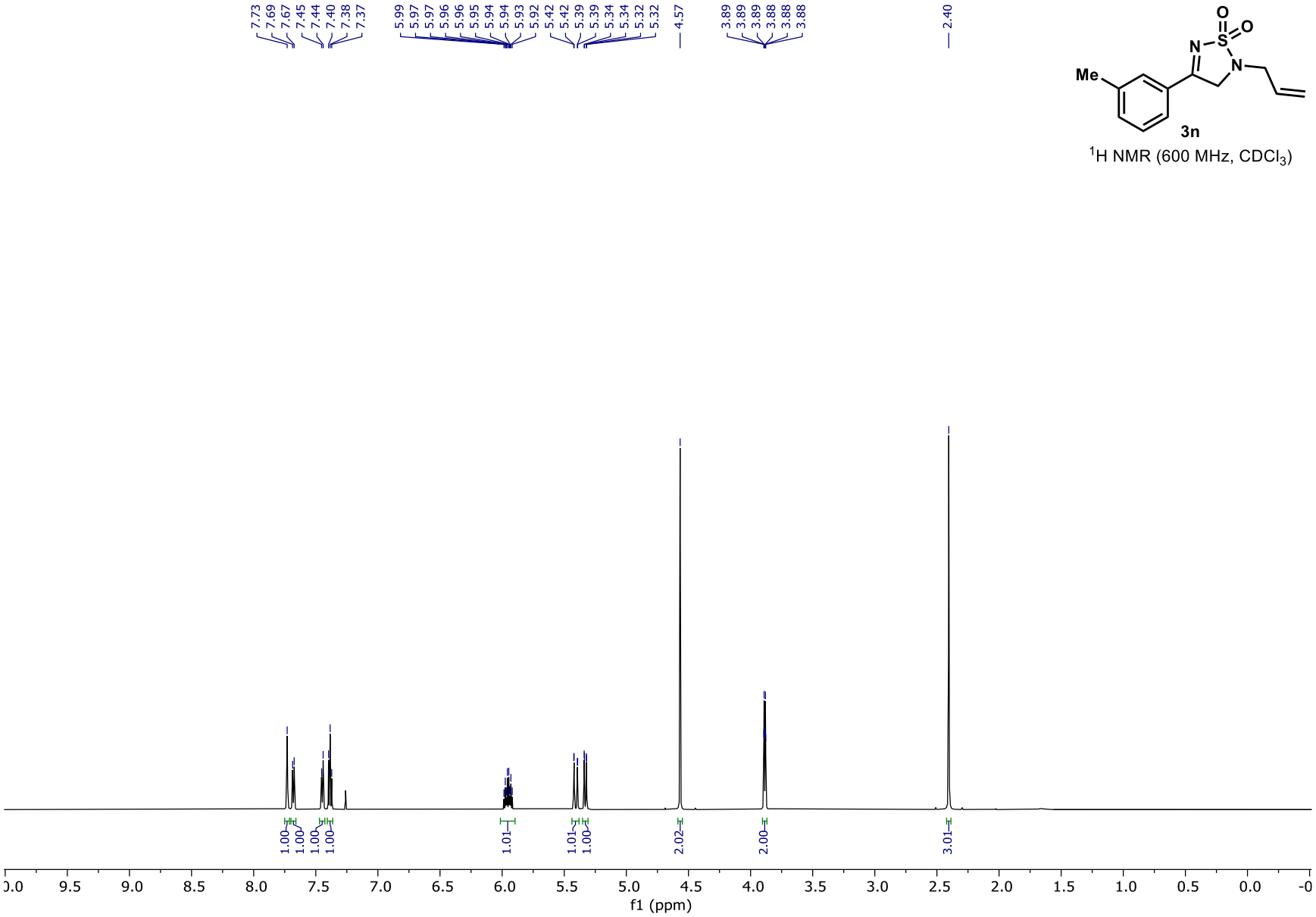
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

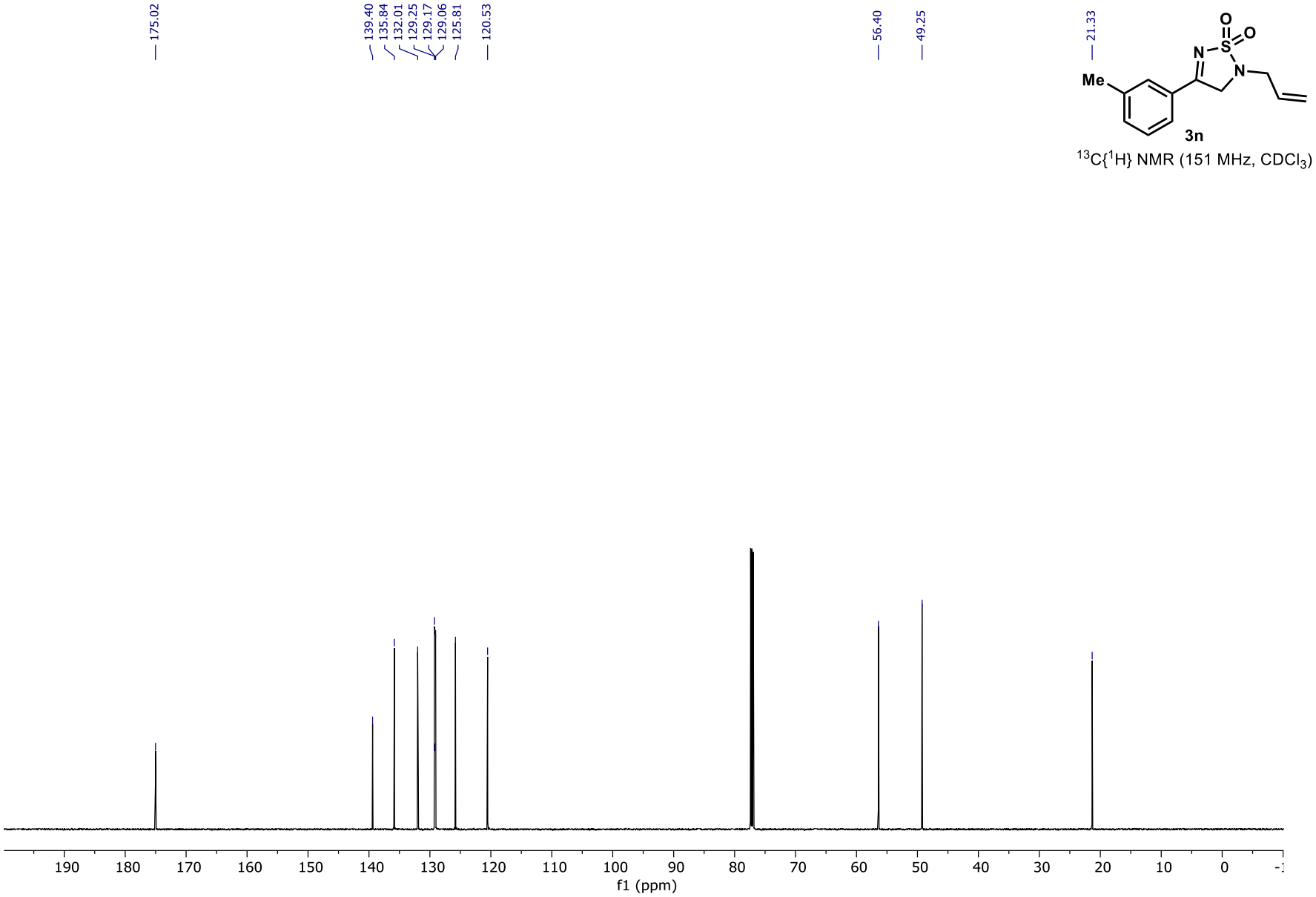


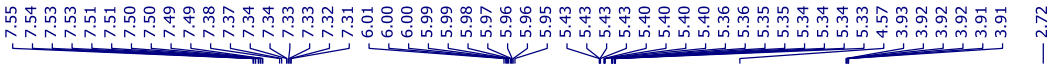
^{1}H NMR (600 MHz, $CDCl_3$)

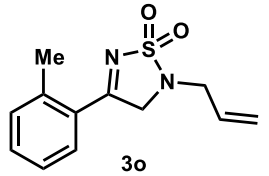


$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)


7.73
7.69
7.67
7.45
7.44
7.40
7.38
7.37
5.99
5.97
5.97
5.96
5.96
5.95
5.94
5.94
5.93
5.92
5.42
5.42
5.39
5.39
5.34
5.34
5.32
5.32
4.57
3.89
3.89
3.89
3.88
3.88
3.88
2.40
Me
3n
1H NMR (600 MHz, CDCl3)
1.00
1.00
1.00
1.00
1.01
1.01
1.00
2.02
2.00
3.01
f1 (ppm)

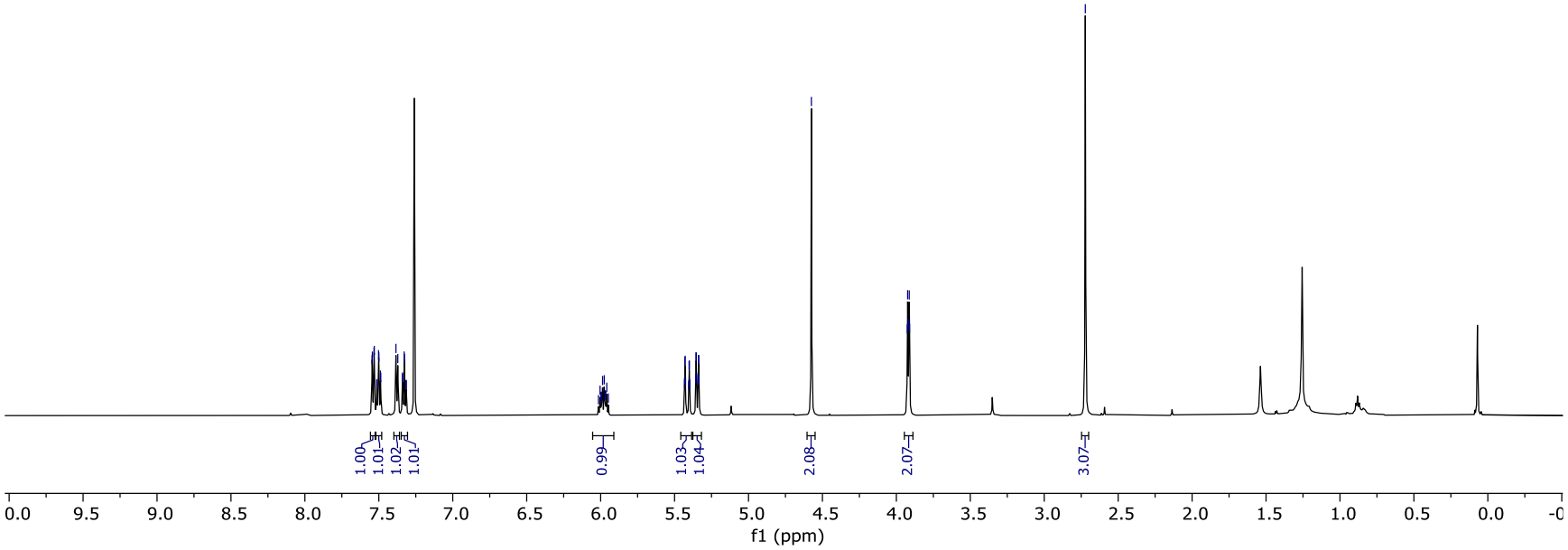

175.02
139.40
135.84
132.01
129.25
129.17
129.06
125.81
120.53
56.40
49.25
21.33
Me
3n
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
f1 (ppm)

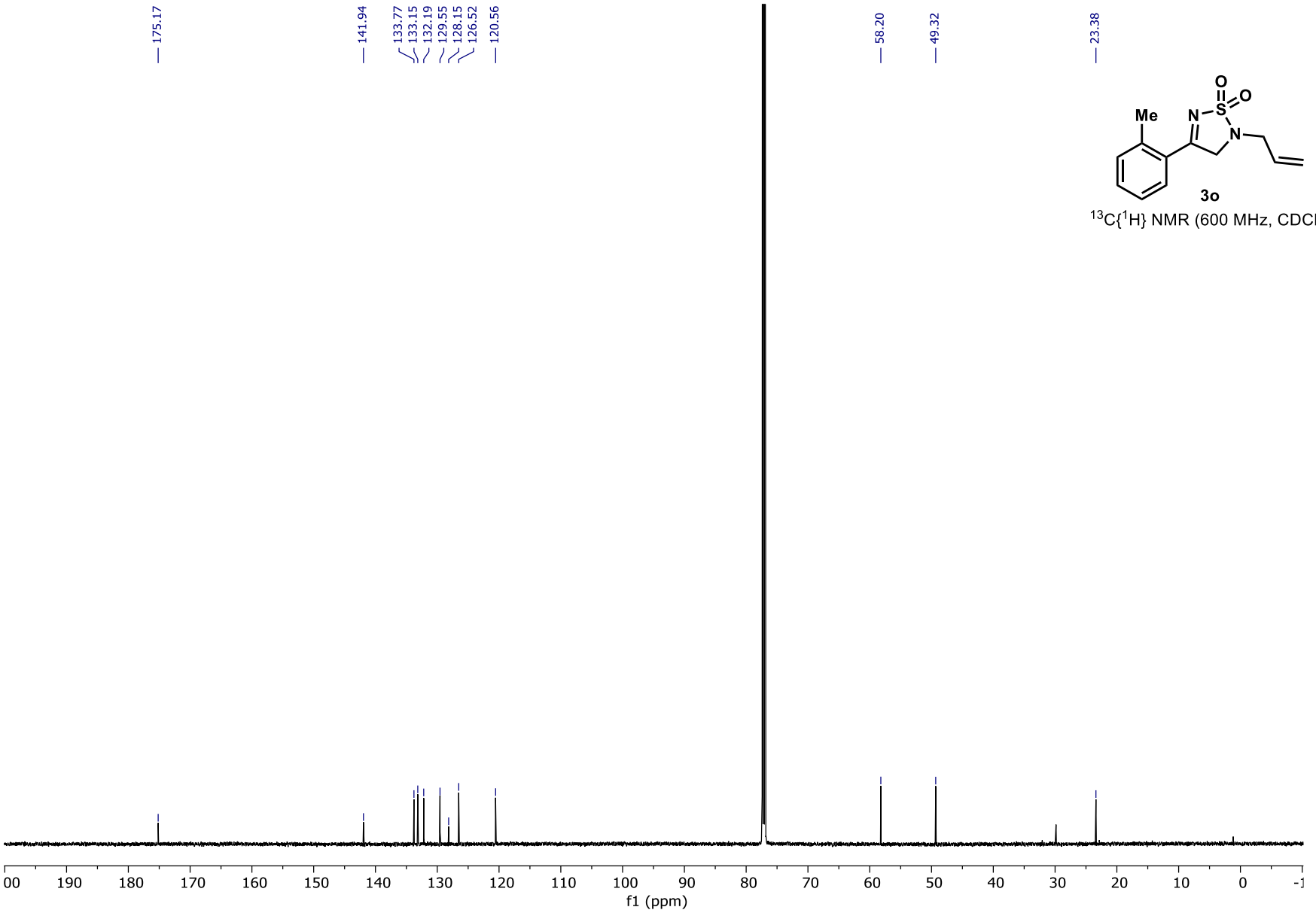


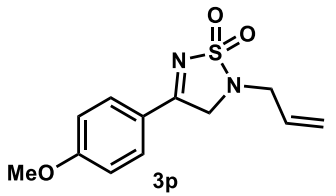


3o

^{1}H NMR (600 MHz, $CDCl_3$)

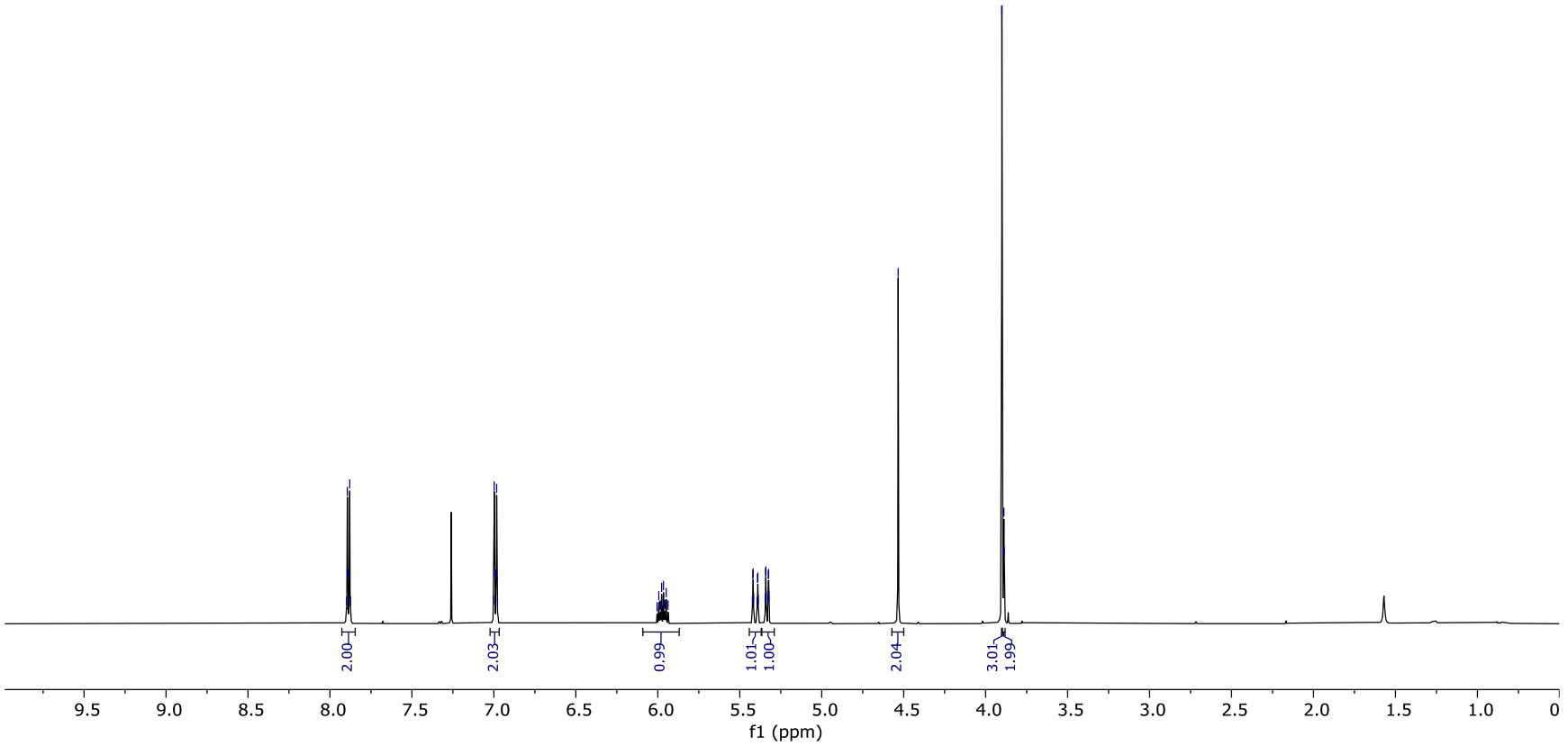


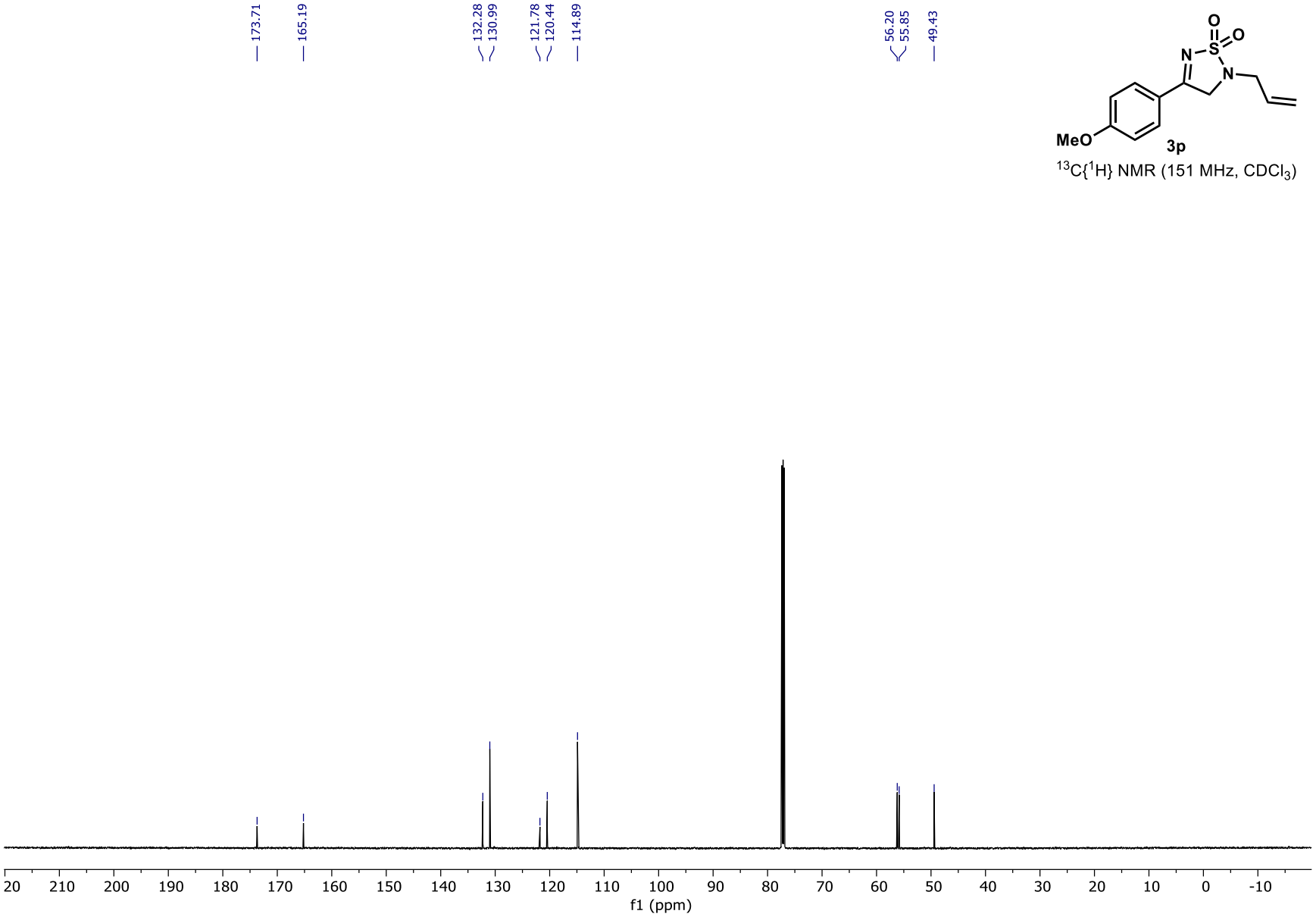

175.17
141.94
133.77
133.15
132.19
129.55
128.15
126.52
120.56
58.20
49.32
23.38
Me
N
S
O
O
N
3o
$^{13}C\{^{1}H\}$ NMR (600 MHz, $CDCl_3$)
f1 (ppm)

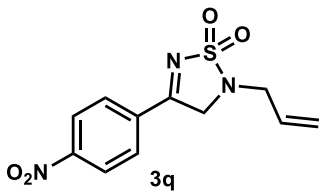


3p

^{1}H NMR (600 MHz, $CDCl_3$)

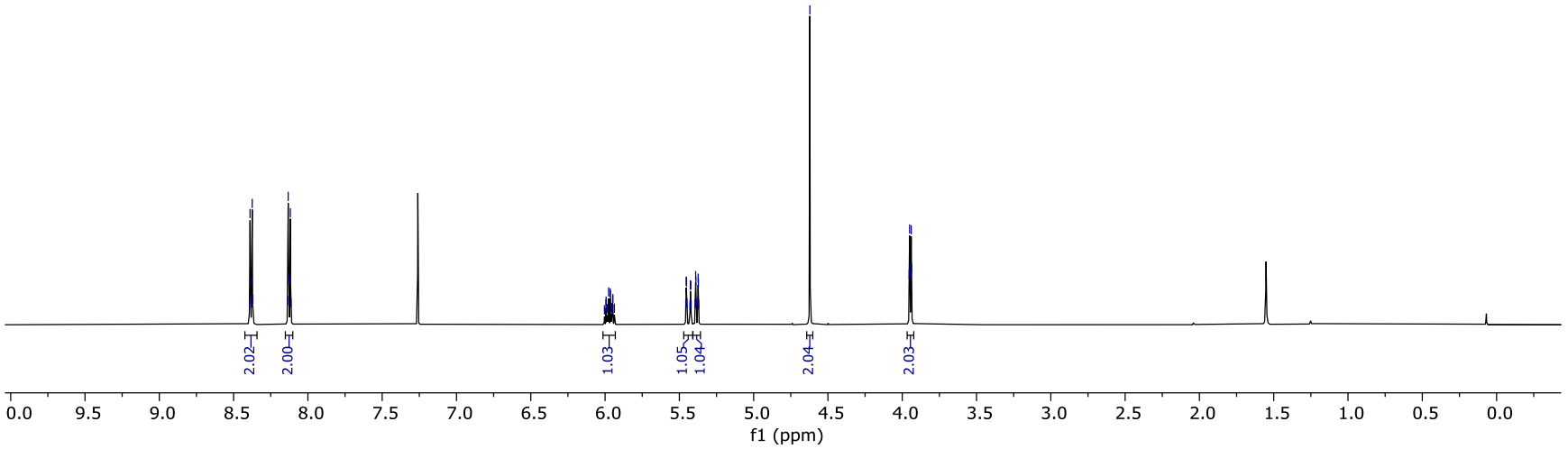


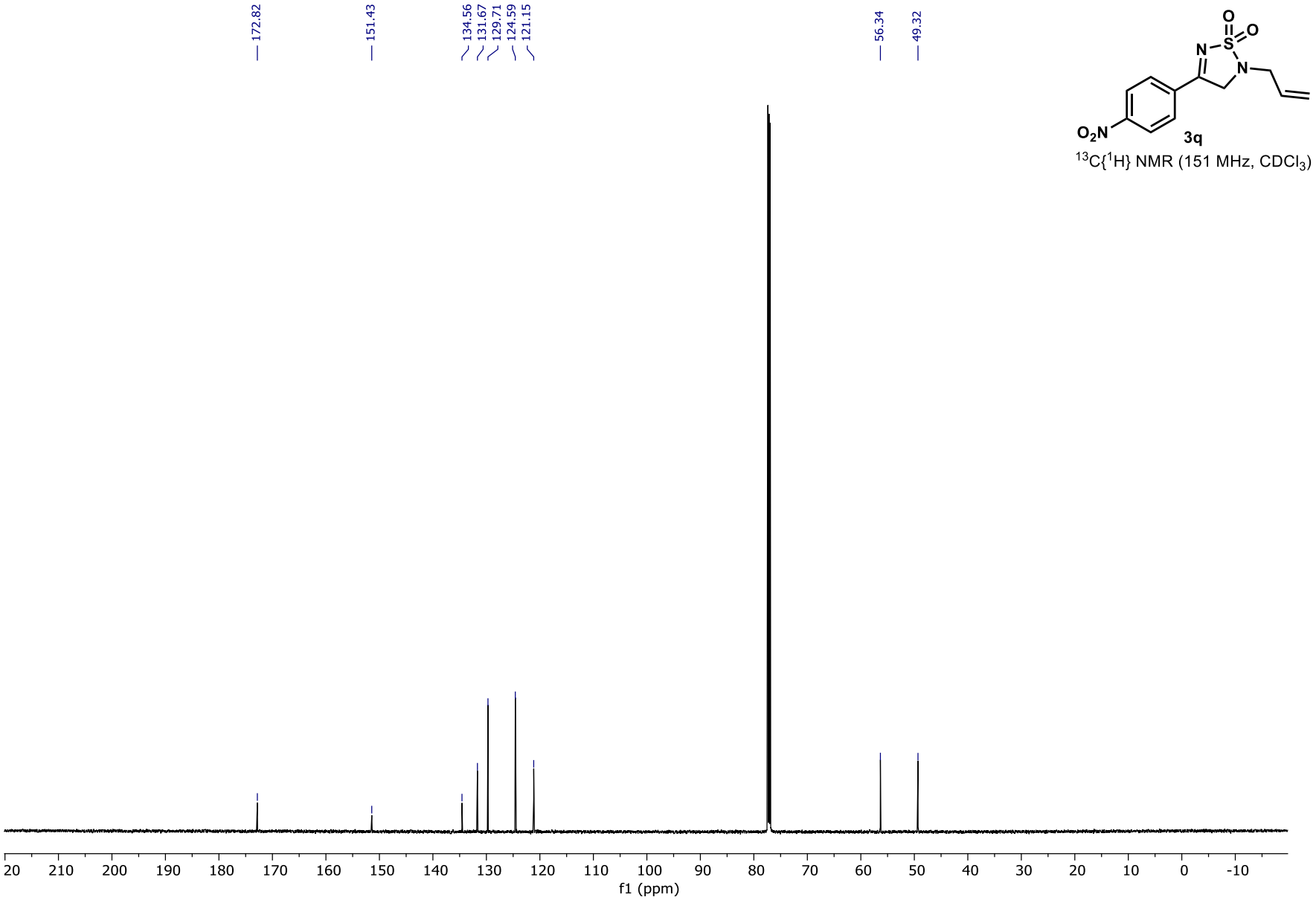

173.71
165.19
132.28
130.99
121.78
120.44
114.89
56.20
55.85
49.43
O
O
N
S
N
MeO
3p
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

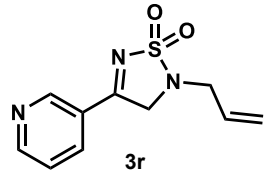


3q

^{1}H NMR (600 MHz, $CDCl_3$)

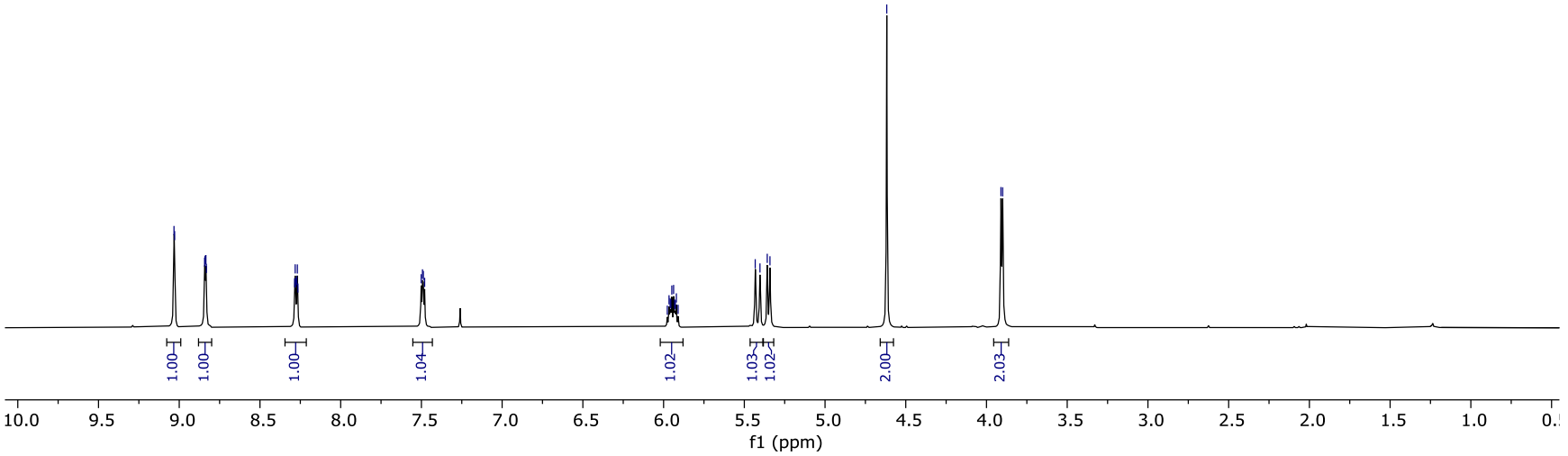


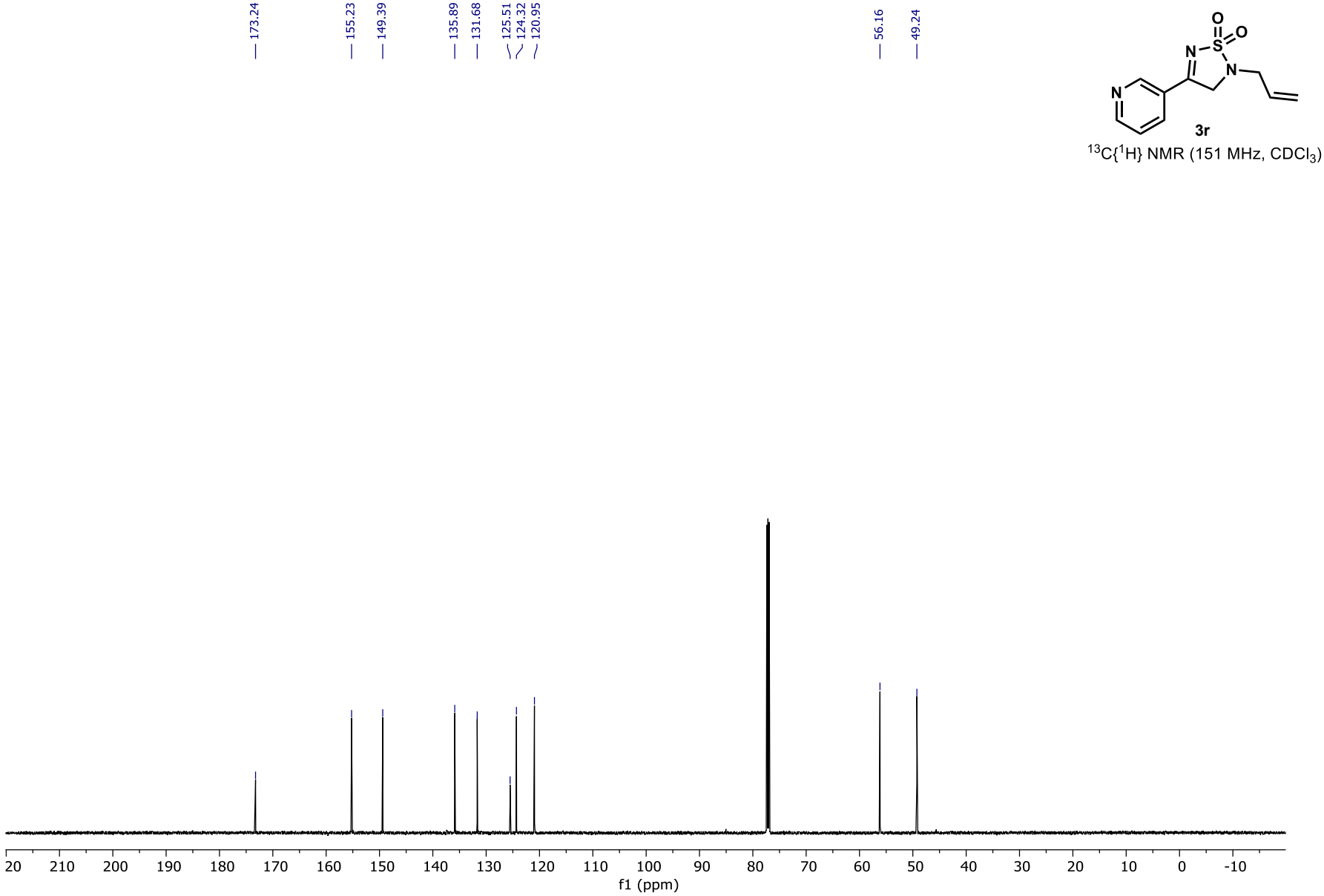

172.82
151.43
134.56
131.67
129.71
124.59
121.15
56.34
49.32
O
O
N
S
N
O_2N
3q
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3r

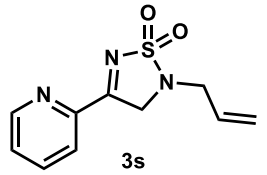
^{1}H NMR (600 MHz, $CDCl_3$)





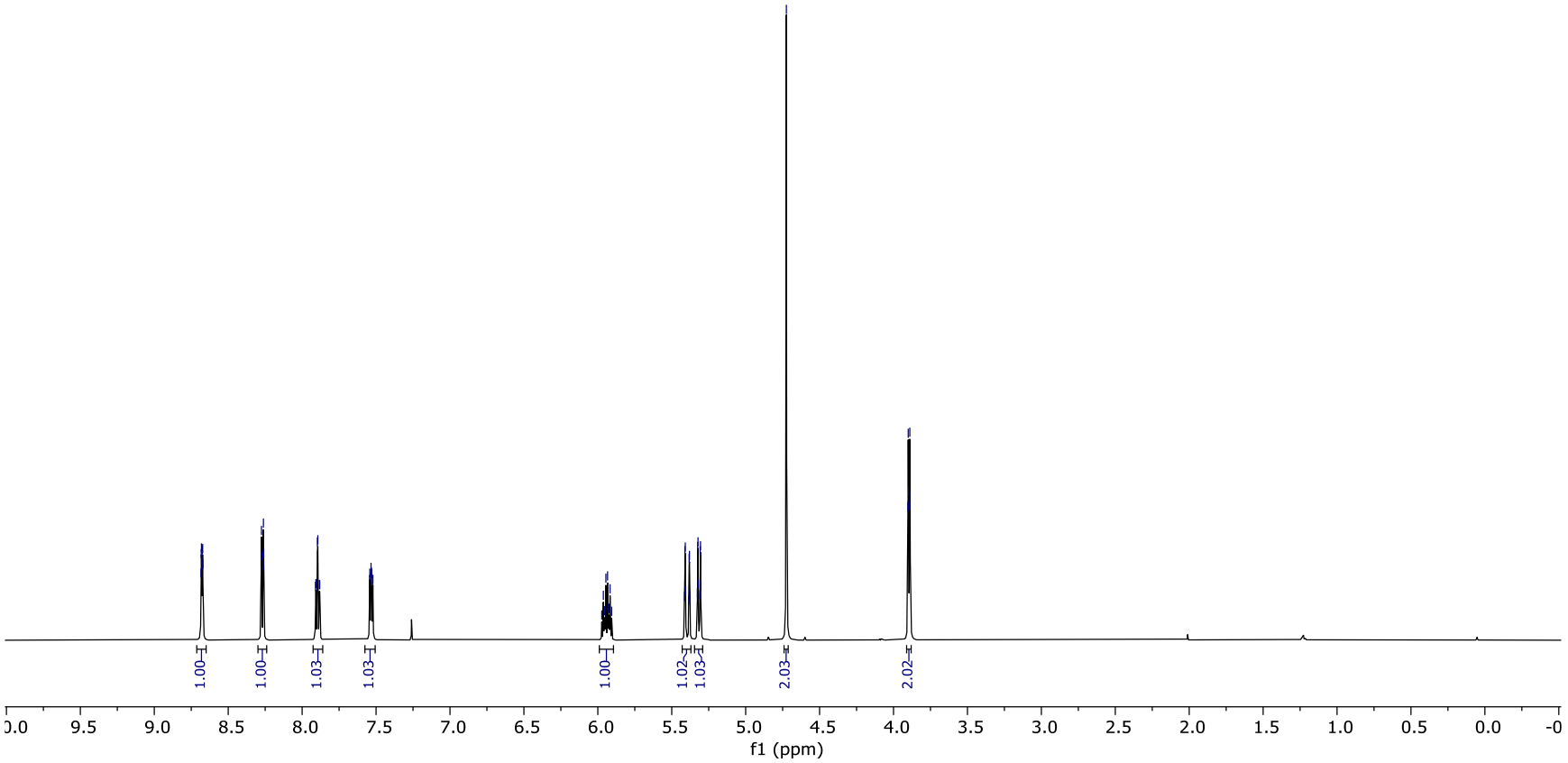
3r

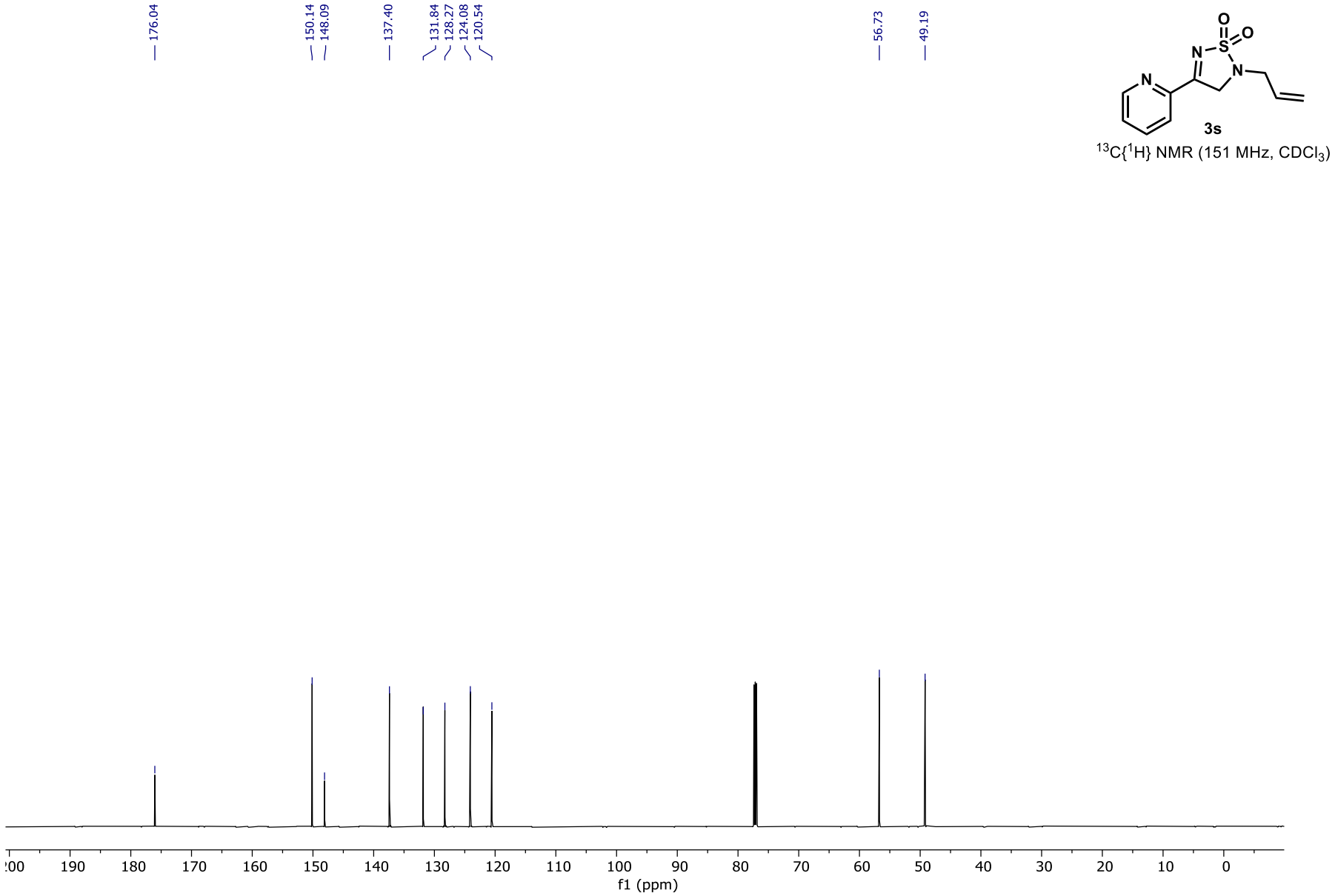
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

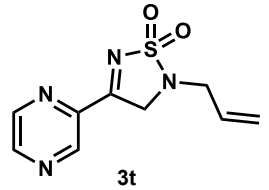


3s

^{1}H NMR (600 MHz, $CDCl_3$)

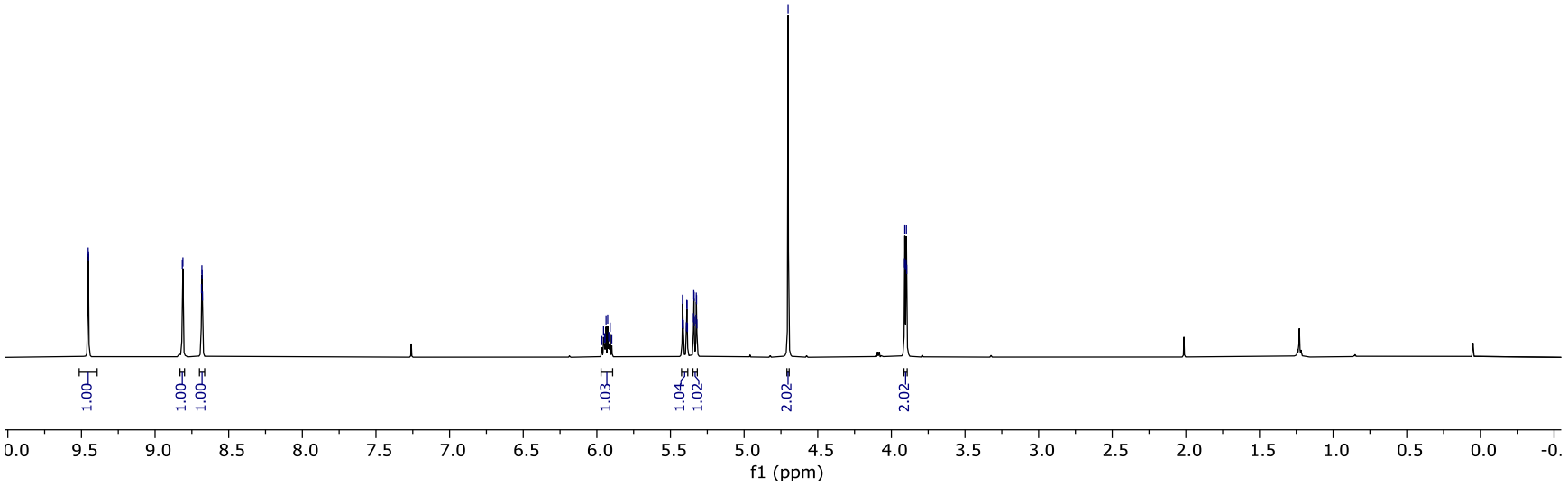


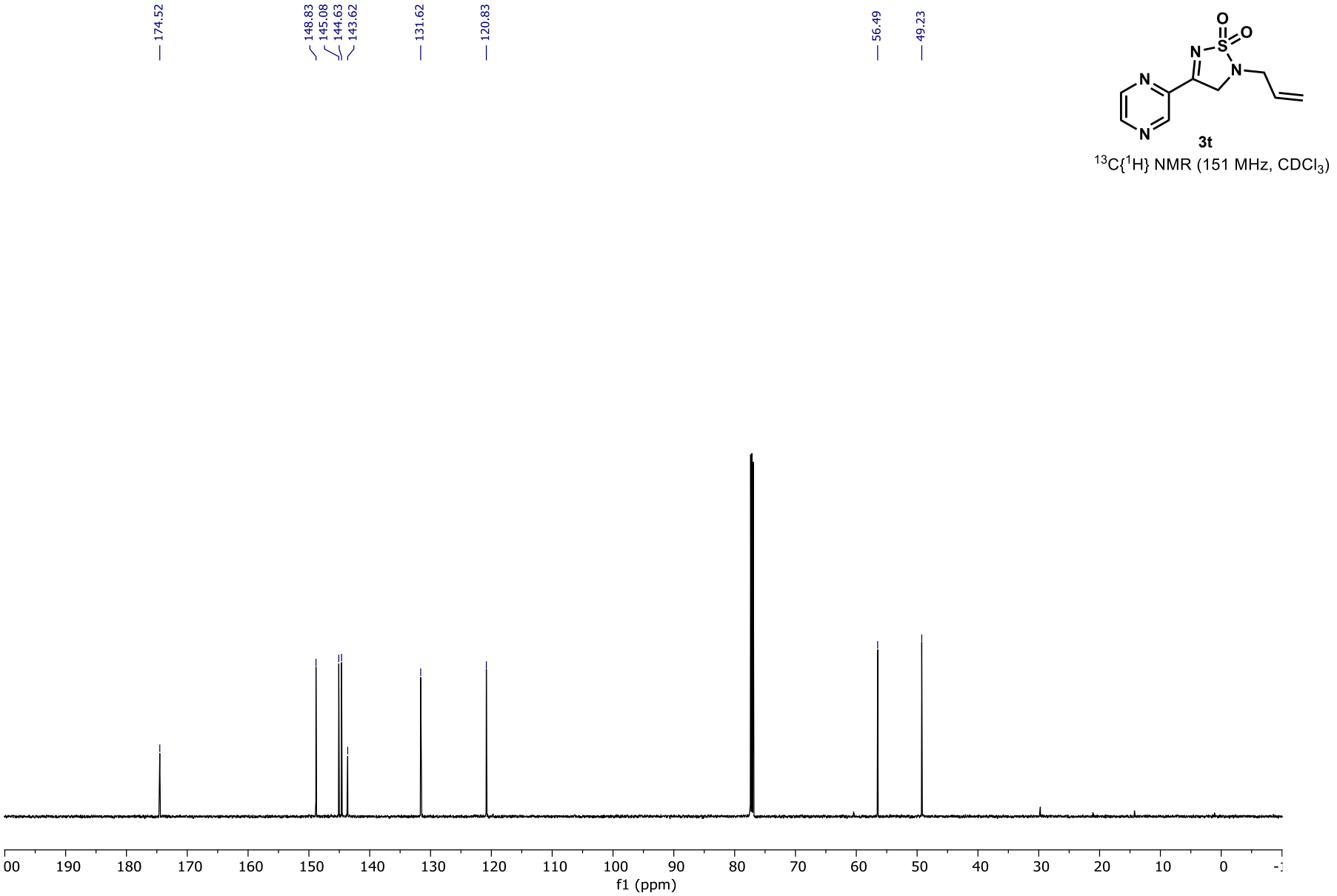

176.04
150.14
148.09
137.40
131.84
128.27
124.08
120.54
56.73
49.19
O
O
N
S
N
N
3s
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

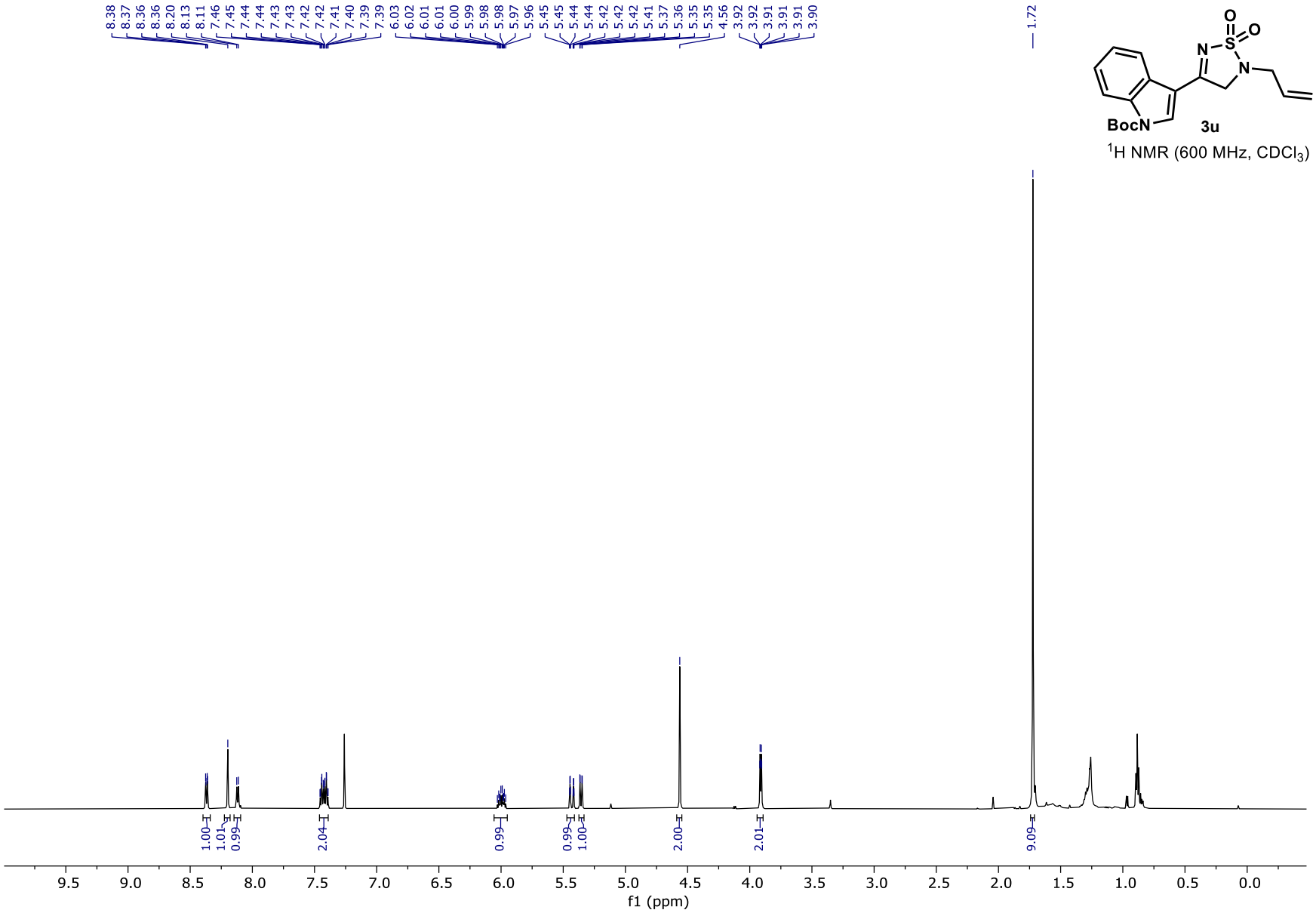


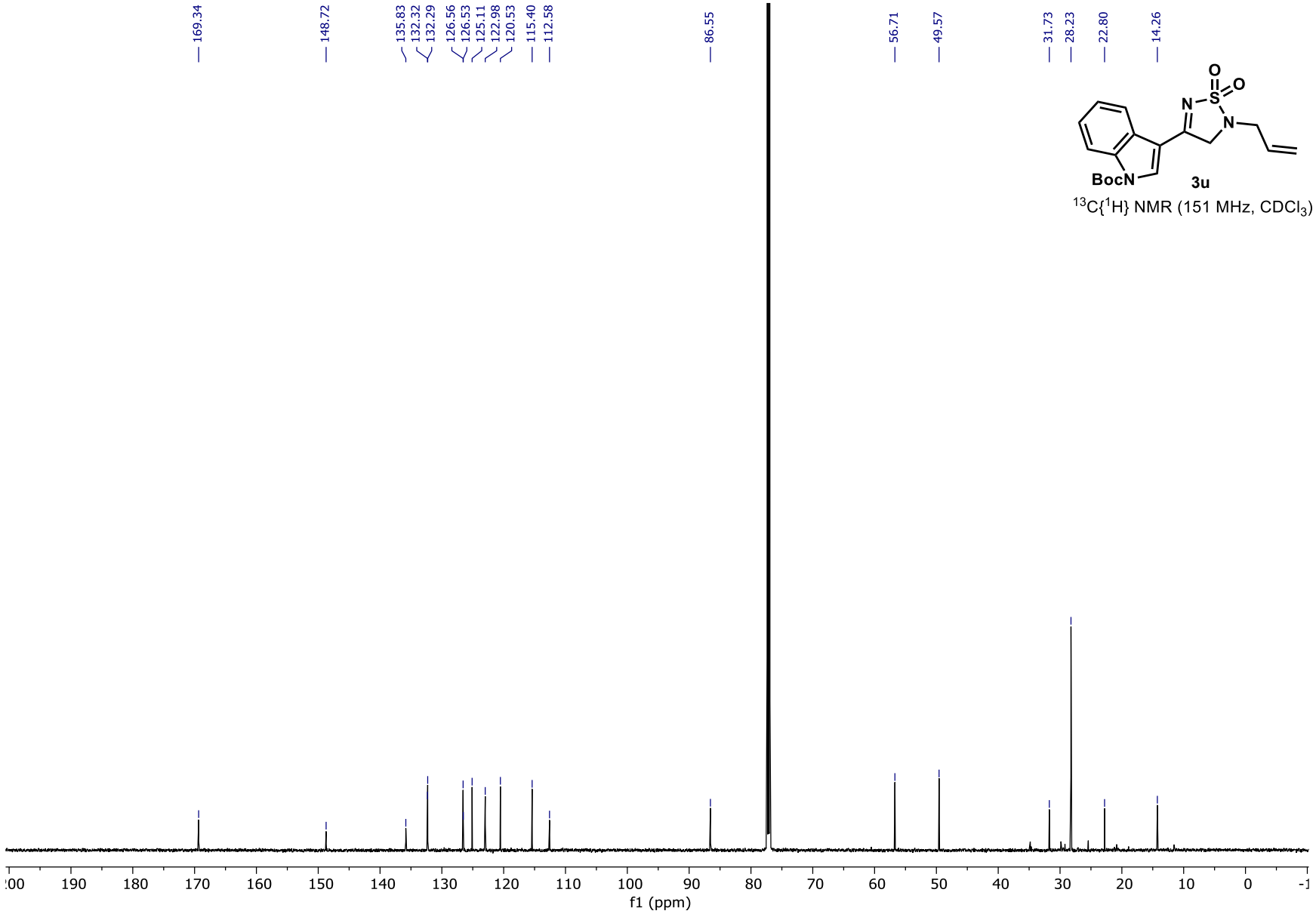
3t

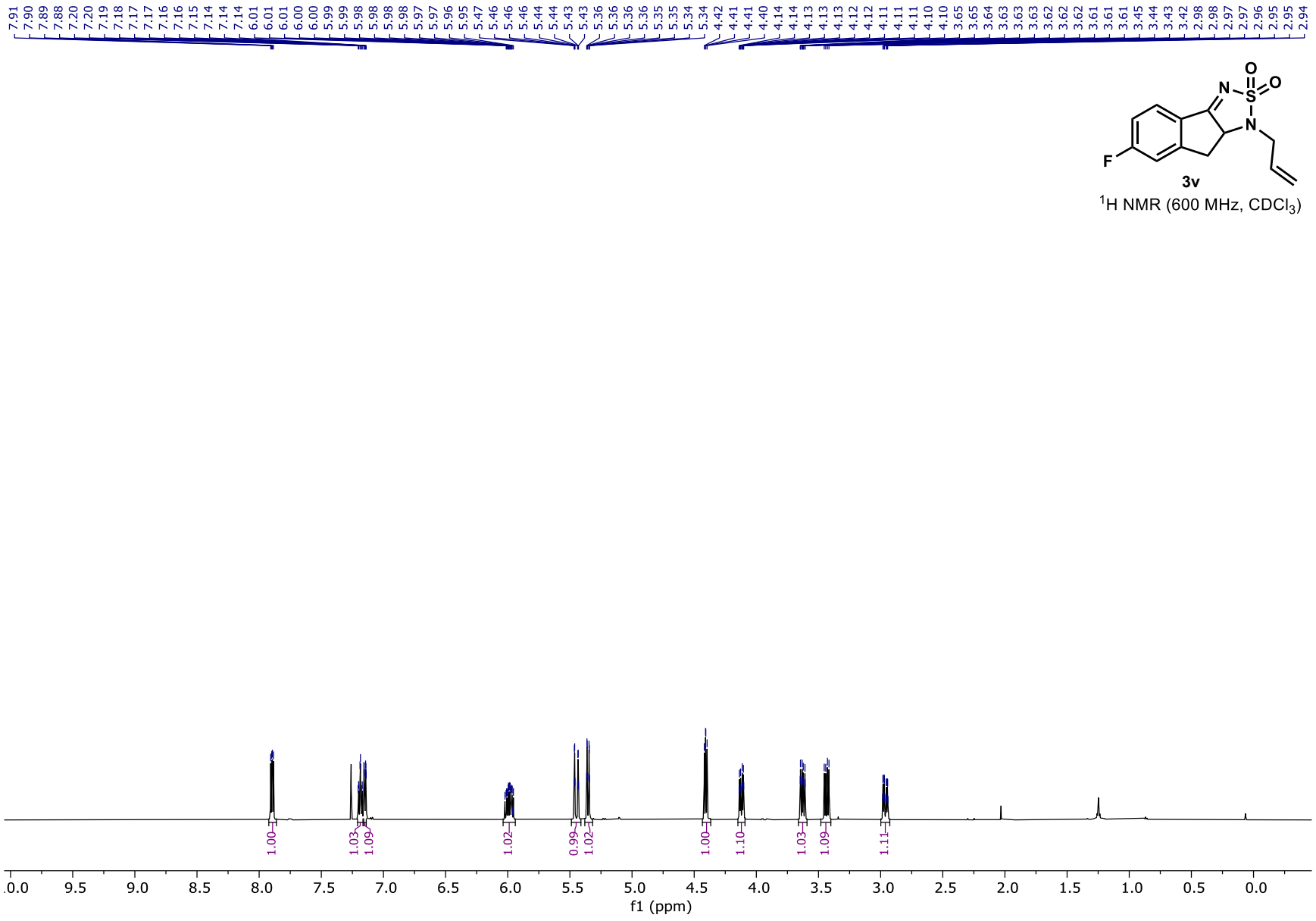
^{1}H NMR (600 MHz, $CDCl_3$)

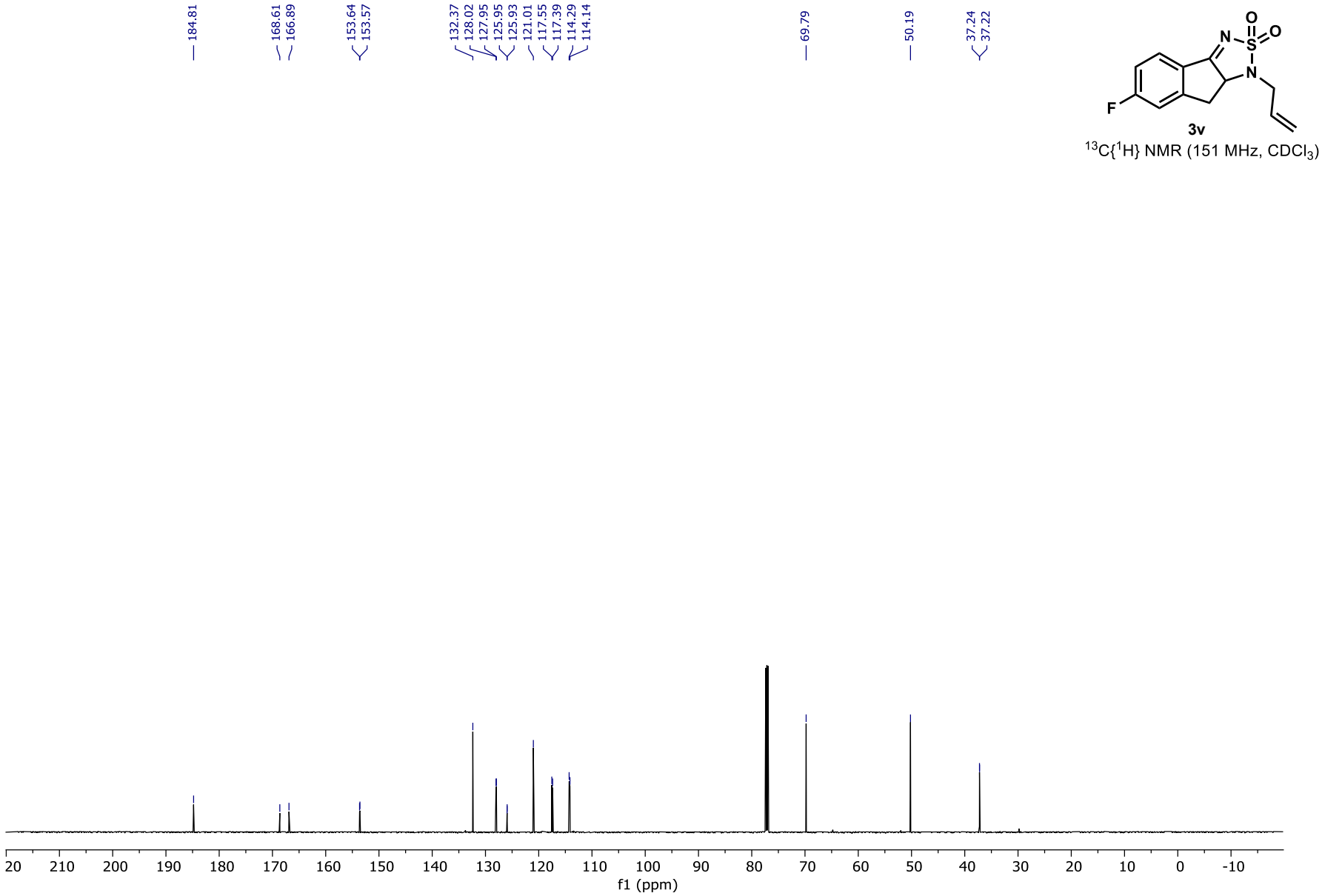


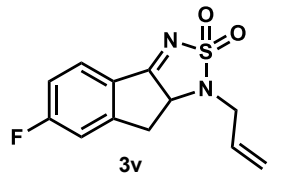

174.52
148.83
145.08
144.63
143.62
131.62
120.83
56.49
49.23
O
O
N
S
N
N
N
3t
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
f1 (ppm)


8.38
8.37
8.36
8.36
8.20
8.13
8.11
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.39
7.39
6.03
6.02
6.01
6.01
6.00
5.99
5.98
5.98
5.97
5.96
5.45
5.45
5.44
5.44
5.42
5.42
5.42
5.41
5.37
5.36
5.35
5.35
4.56
3.92
3.92
3.91
3.91
3.91
3.90
1.72
1.00
1.01
0.99
2.04
0.99
0.99
1.00
2.00
2.01
9.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
O
S
N
N
BocN
3u
^{1}H NMR (600 MHz, $CDCl_3$)


169.34
148.72
135.83
132.32
132.29
126.56
126.53
125.11
122.98
120.53
115.40
112.58
86.55
56.71
49.57
31.73
28.23
22.80
14.26
O
O
N
S
N
BocN
3u
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
f1 (ppm)

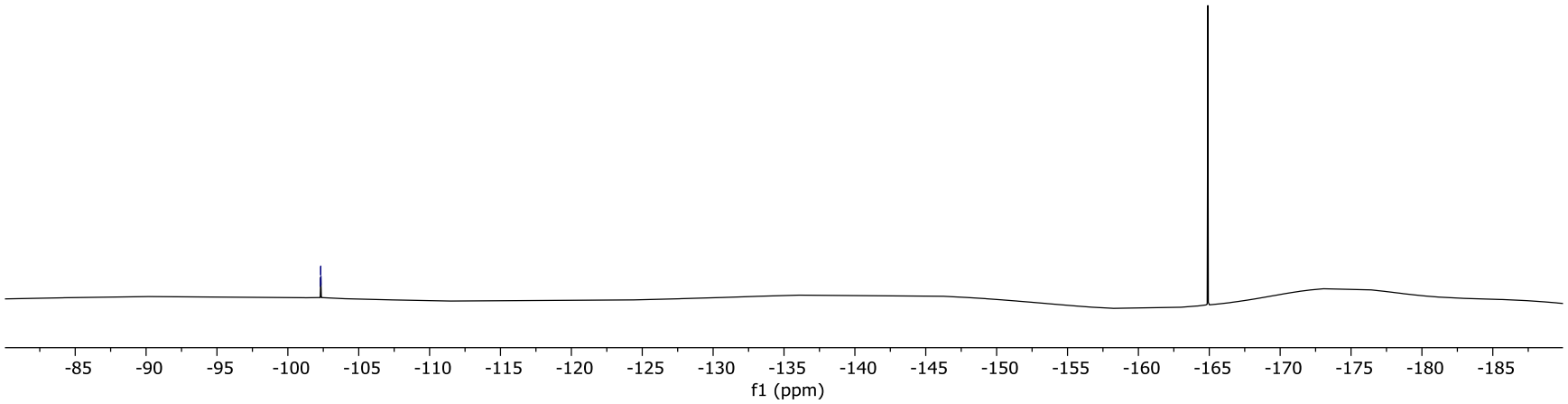

7.91 7.90 7.89 7.88 7.20 7.20 7.19 7.18 7.17 7.17 7.16 7.16 7.15 7.14 7.14 7.14 6.01 6.01 6.00 6.00 5.99 5.99 5.98 5.98 5.98 5.98 5.97 5.97 5.96 5.95 5.47 5.46 5.46 5.44 5.44 5.43 5.43 5.36 5.36 5.36 5.35 5.35 5.34 5.34 4.42 4.41 4.41 4.40 4.14 4.14 4.13 4.13 4.13 4.12 4.12 4.11 4.11 4.11 4.10 4.10 3.65 3.65 3.64 3.63 3.63 3.63 3.62 3.62 3.62 3.61 3.61 3.61 3.45 3.44 3.43 3.42 2.98 2.98 2.97 2.97 2.96 2.95 2.95 2.94
O
N
S
O
N
F
3v
1H NMR (600 MHz, CDCl3)
1.00
1.03
1.09
1.02
0.99
1.02
1.00
1.10
1.03
1.09
1.11
.0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

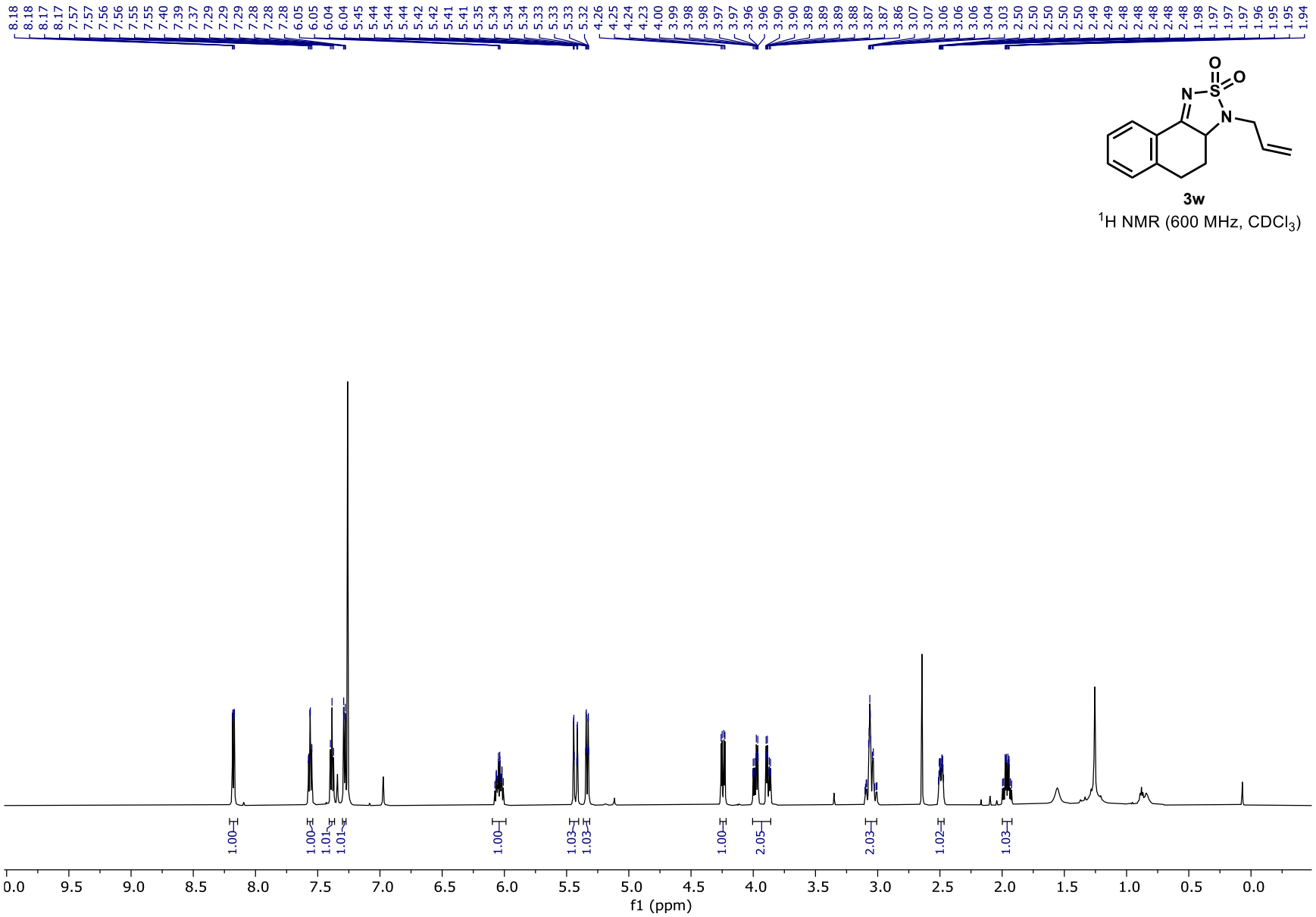

184.81
168.61
166.89
153.64
153.57
132.37
128.02
127.95
125.95
125.93
121.01
117.55
117.39
114.29
114.14
69.79
50.19
37.24
37.22
O
N
S
O
N
F
3v
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3v

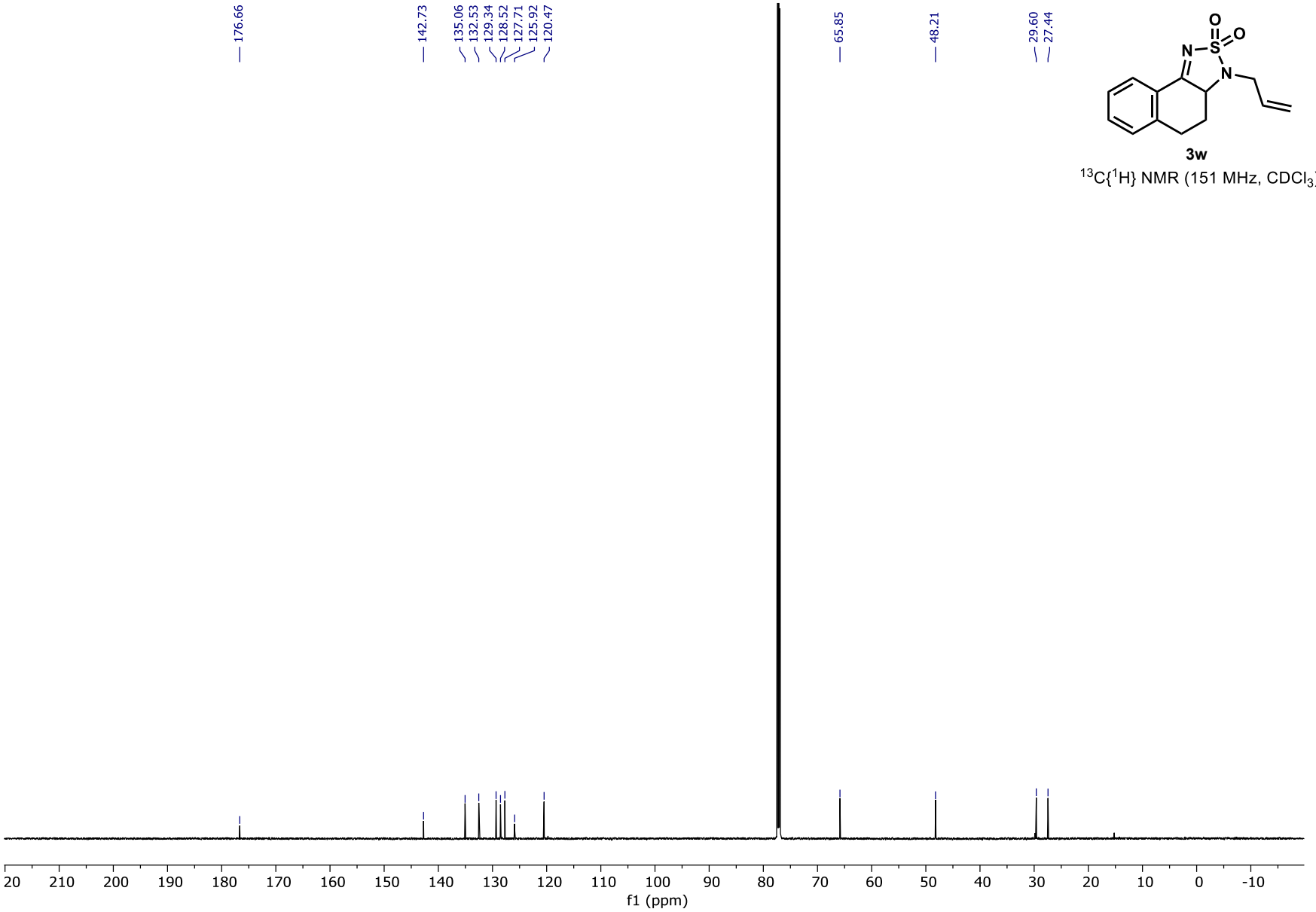
$^{19}F\{^{1}H\}$ NMR (565 MHz, $CDCl_3$)





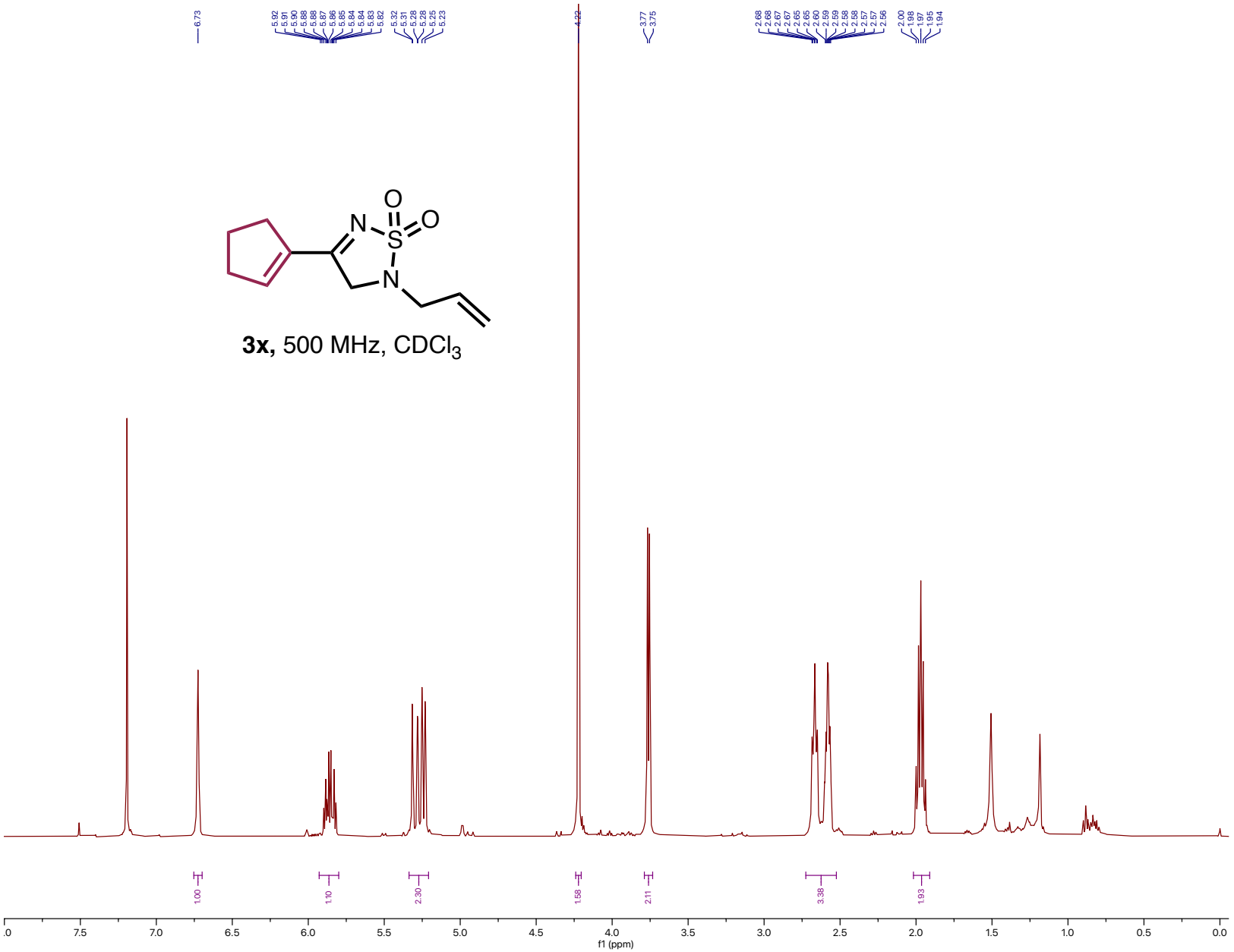
3w

^{1}H NMR (600 MHz, $CDCl_3$)

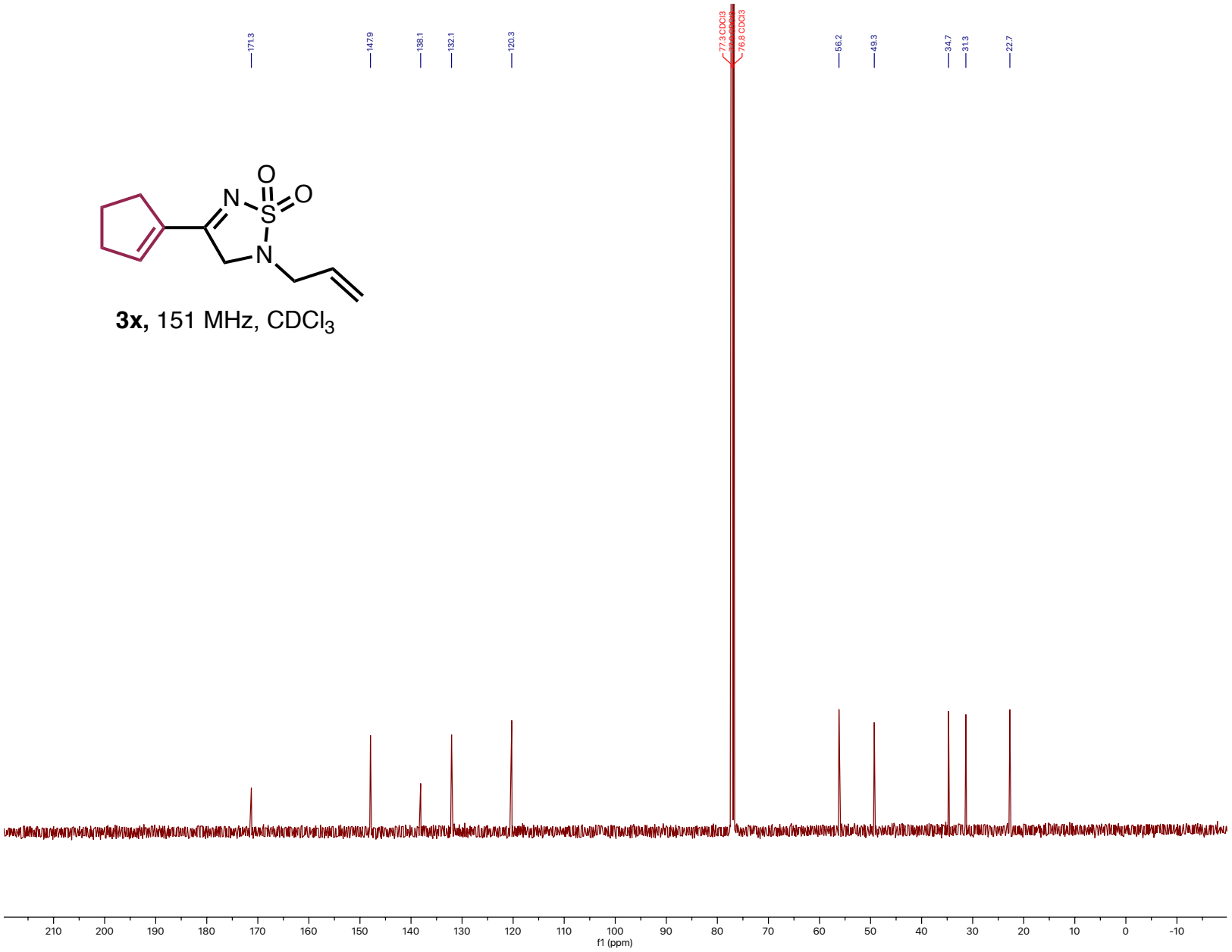


3w

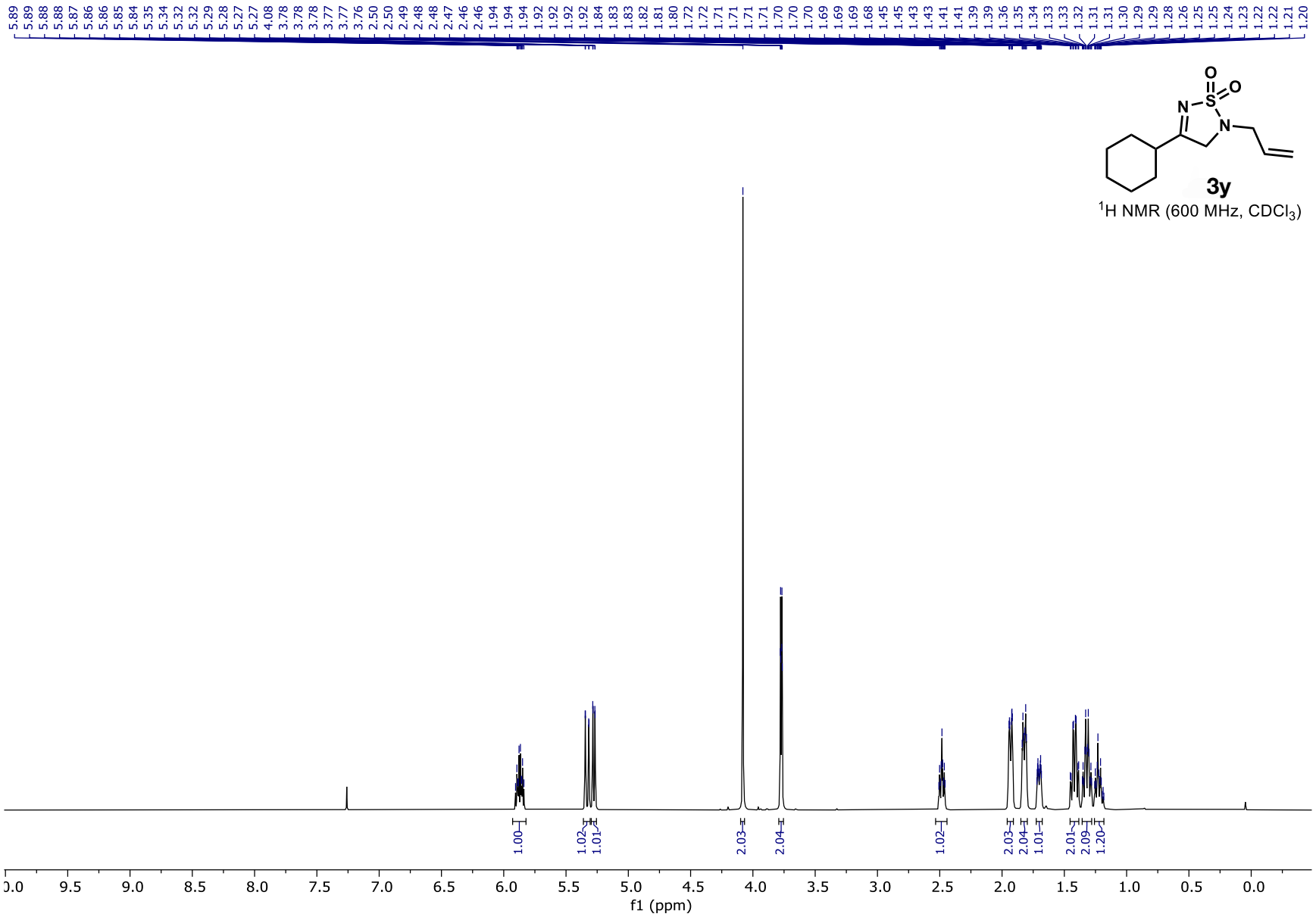
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

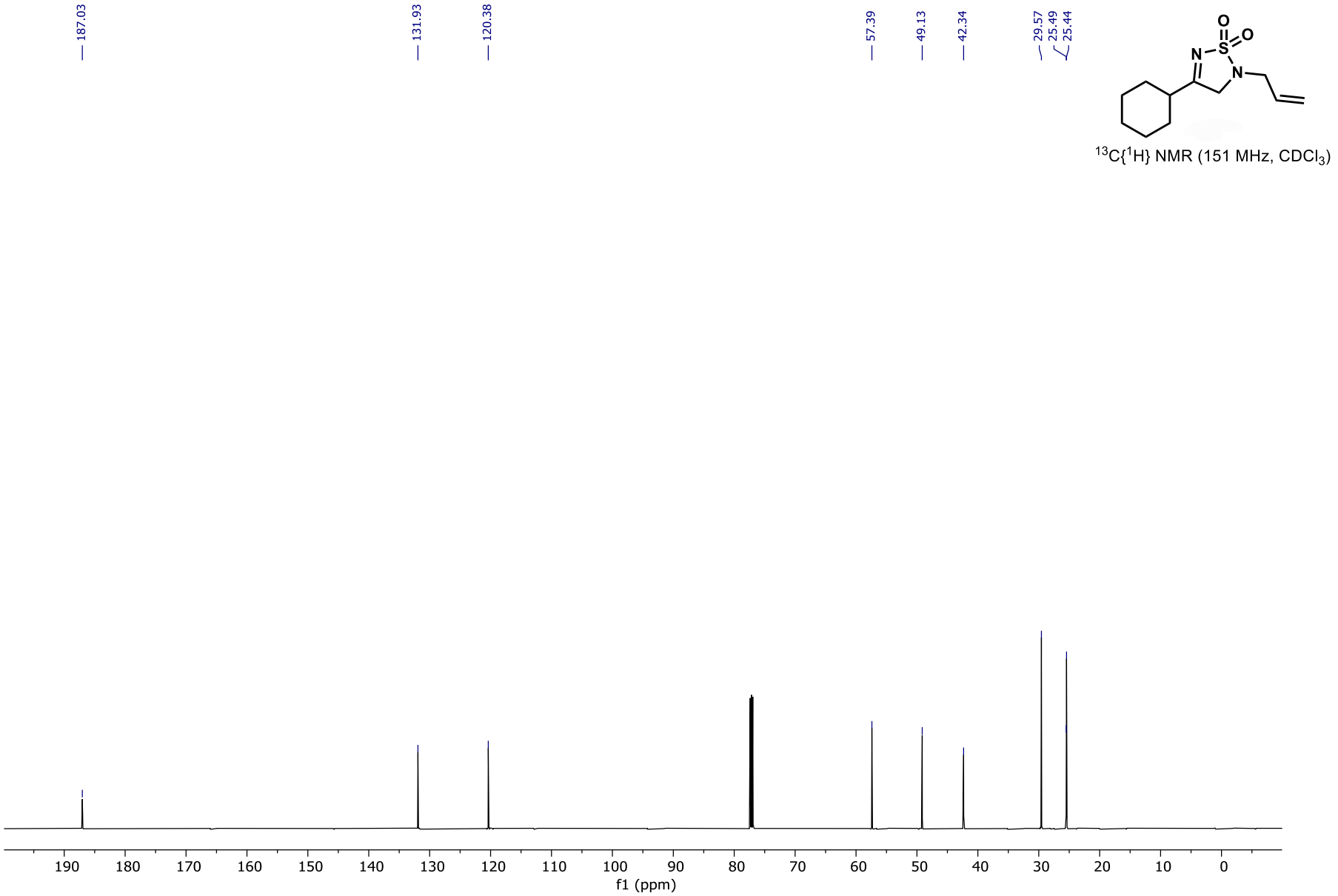


3x, 500 MHz, $CDCl_3$

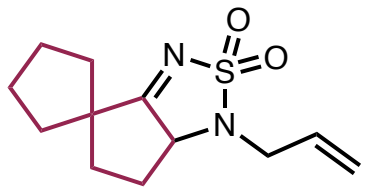


3x, 151 MHz, $CDCl_3$

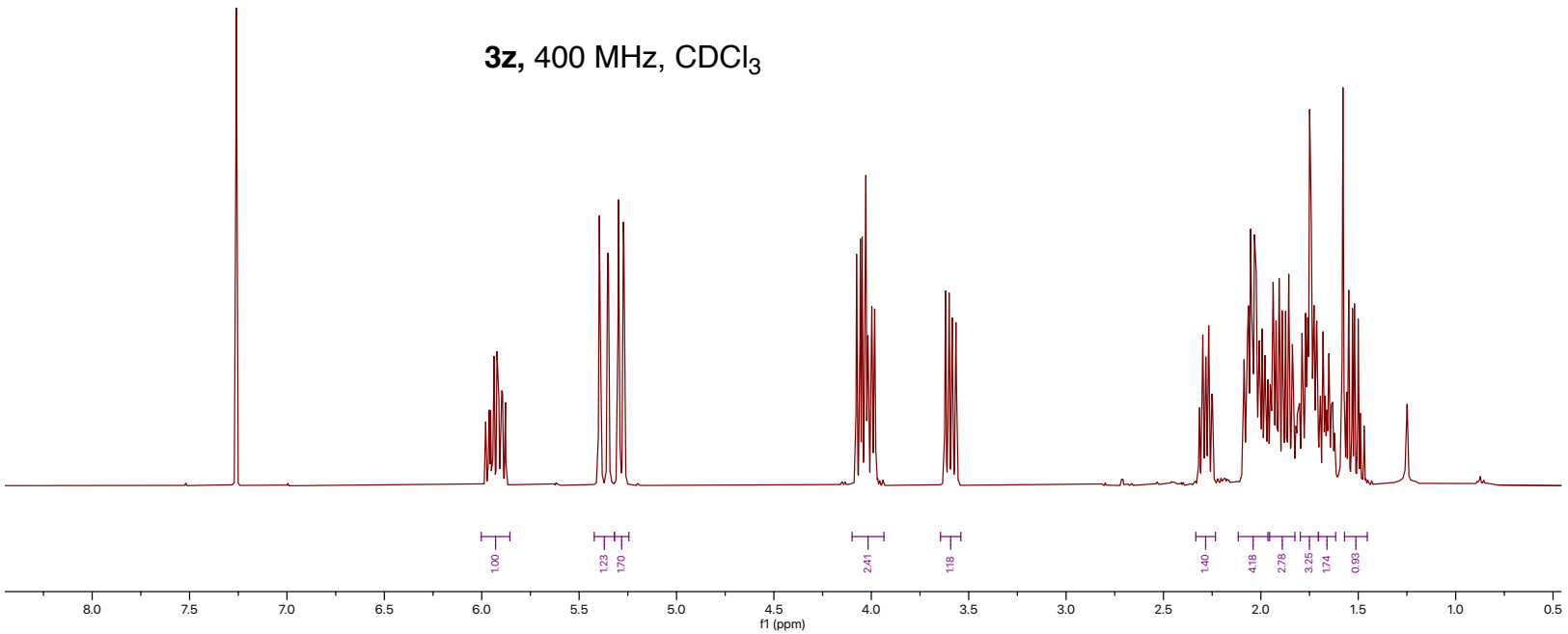

5.89 5.89 5.88 5.88 5.87 5.86 5.86 5.85 5.84 5.35 5.34 5.32 5.32 5.29 5.28 5.27 5.27 4.08 3.78 3.78 3.78 3.77 3.77 3.76 2.50 2.50 2.49 2.48 2.48 2.47 2.46 2.46 1.94 1.94 1.94 1.92 1.92 1.92 1.84 1.83 1.83 1.82 1.81 1.80 1.72 1.72 1.71 1.71 1.71 1.71 1.70 1.70 1.70 1.69 1.69 1.69 1.68 1.45 1.45 1.43 1.43 1.41 1.41 1.39 1.39 1.36 1.35 1.34 1.33 1.33 1.32 1.31 1.31 1.30 1.29 1.29 1.28 1.26 1.25 1.25 1.24 1.23 1.22 1.22 1.21 1.20
O
O
N
S
N
3y
1H NMR (600 MHz, CDCl3)
1.00
1.02
1.01
2.03
2.04
1.02
2.03
2.04
1.01
2.01
2.09
1.20
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

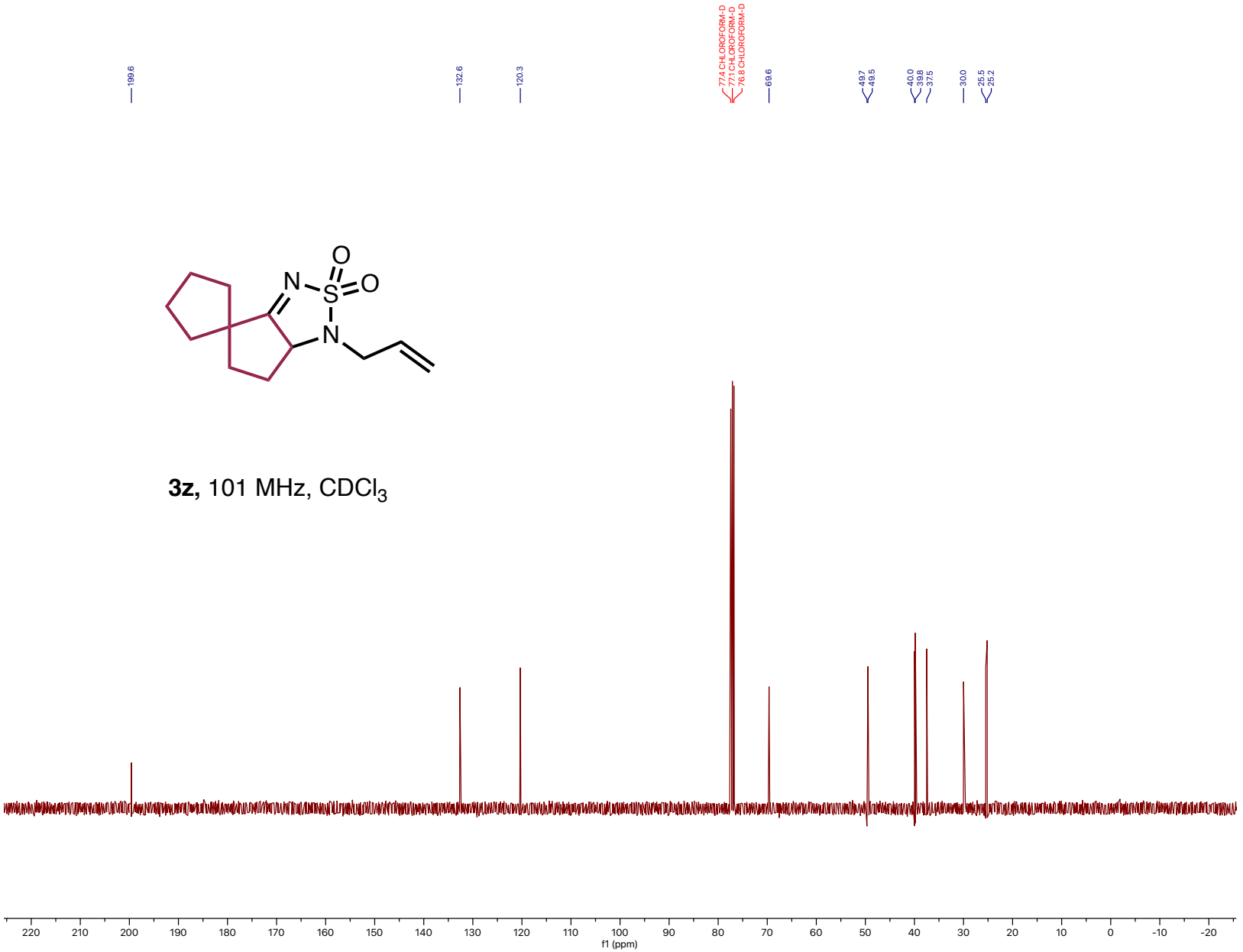


$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

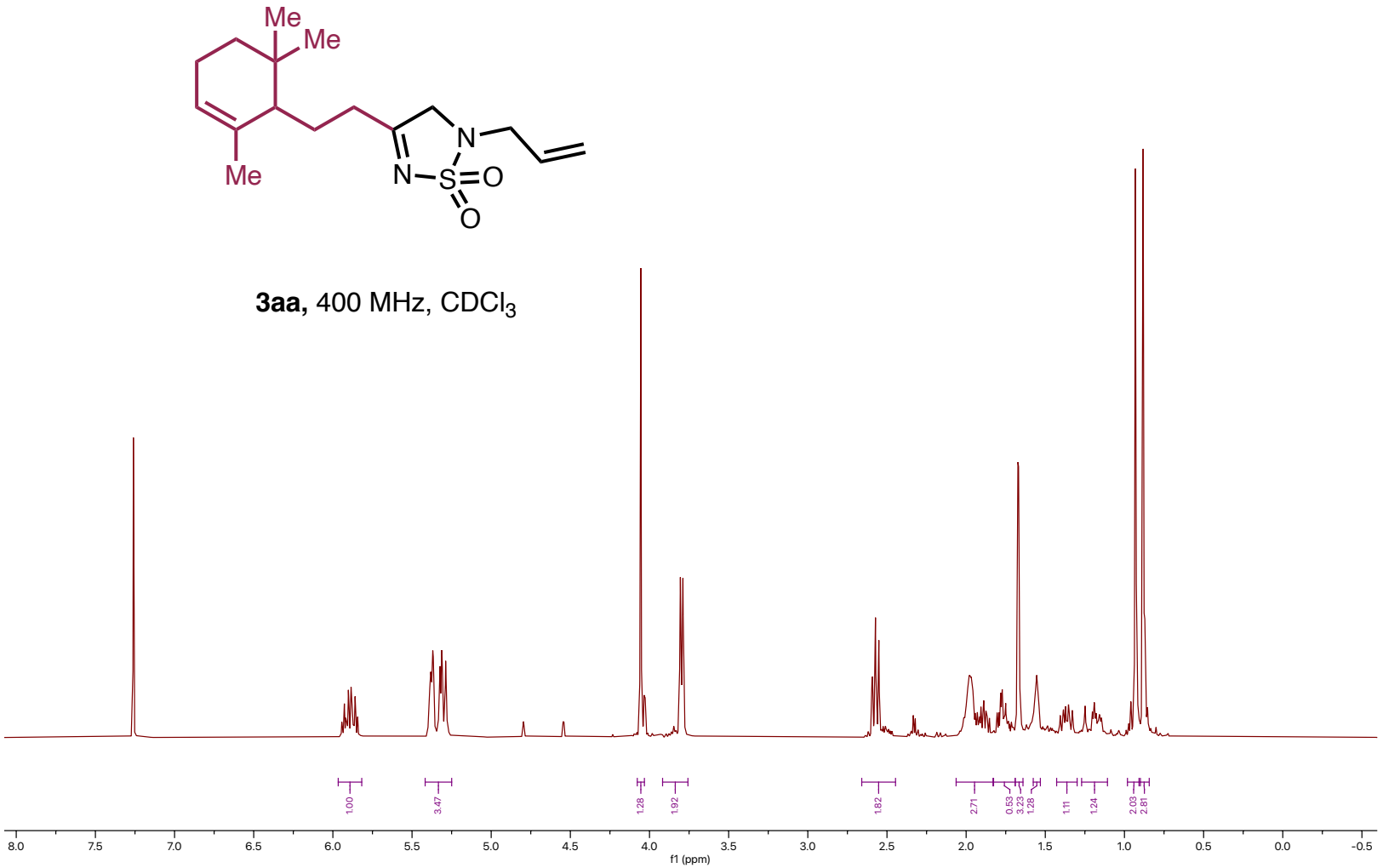


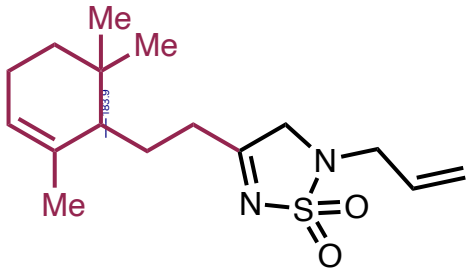
3z, 400 MHz, $CDCl_3$



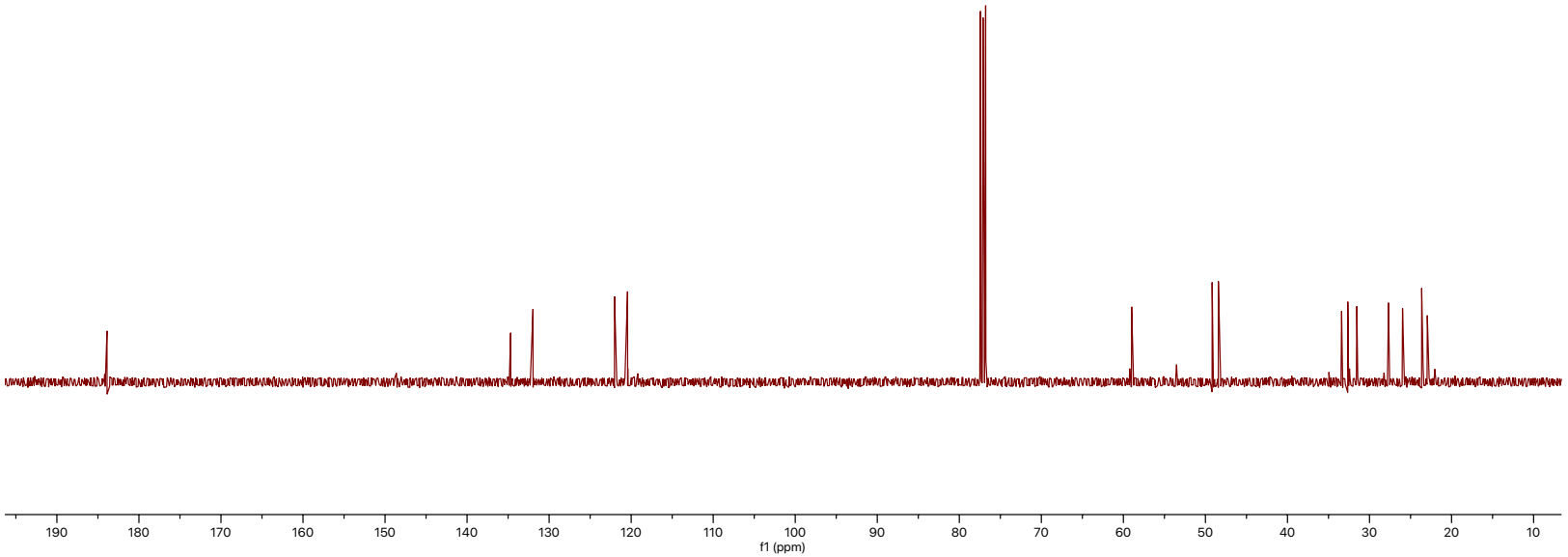


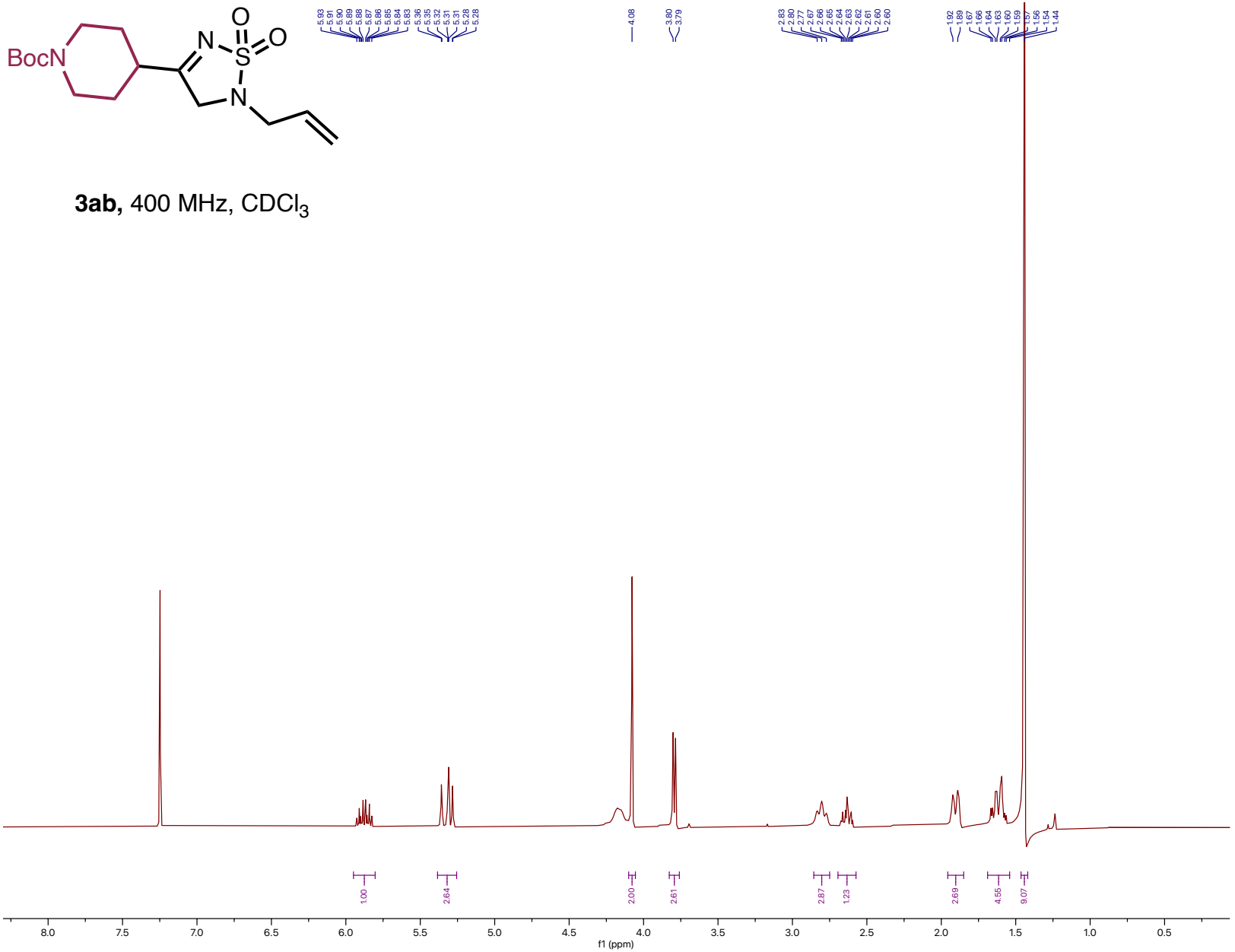
3z, 101 MHz, $CDCl_3$


Me
Me
Me
N
N
S
O
O
3aa, 400 MHz, CDCl3
f1 (ppm)

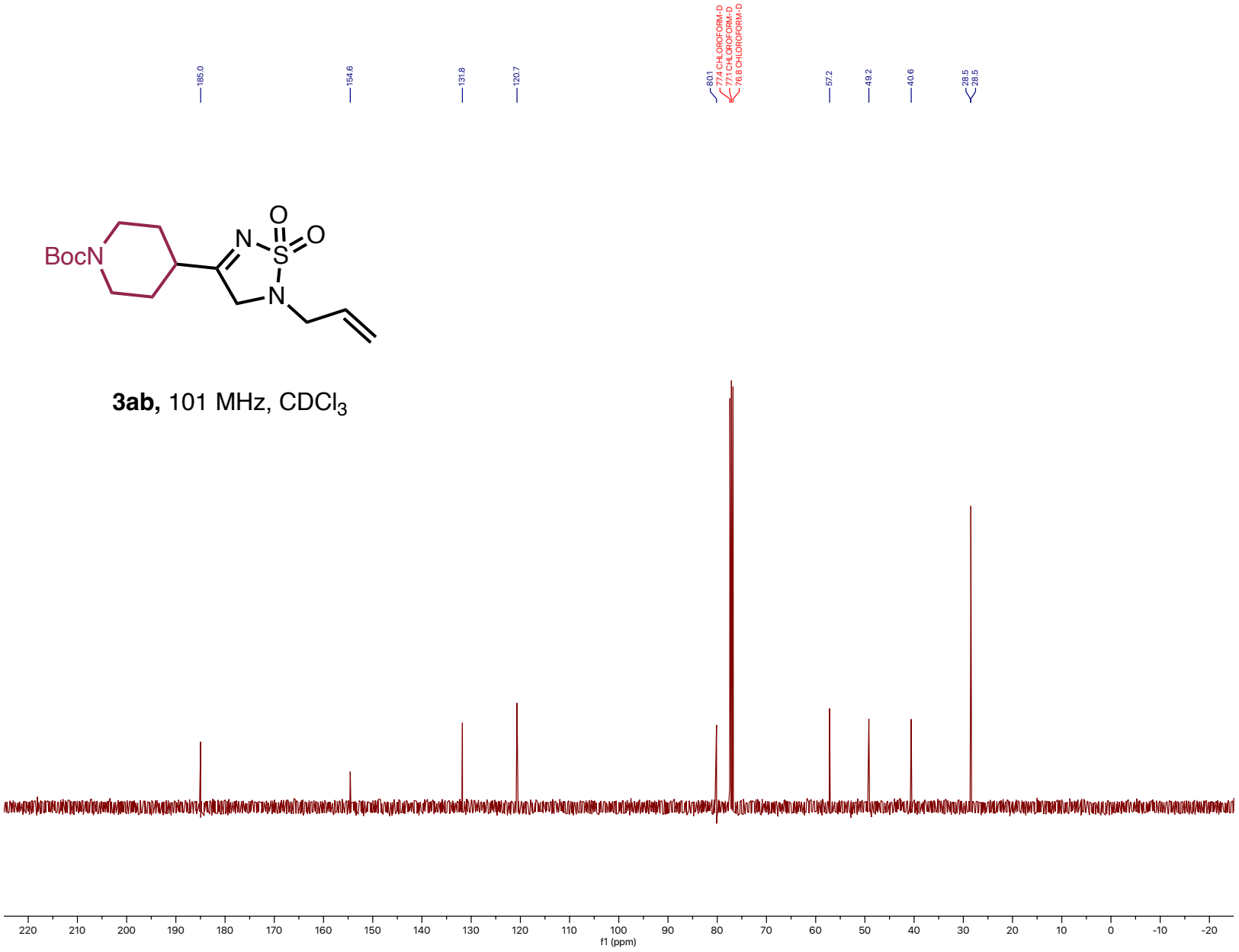


3aa, 101 MHz, $CDCl_3$

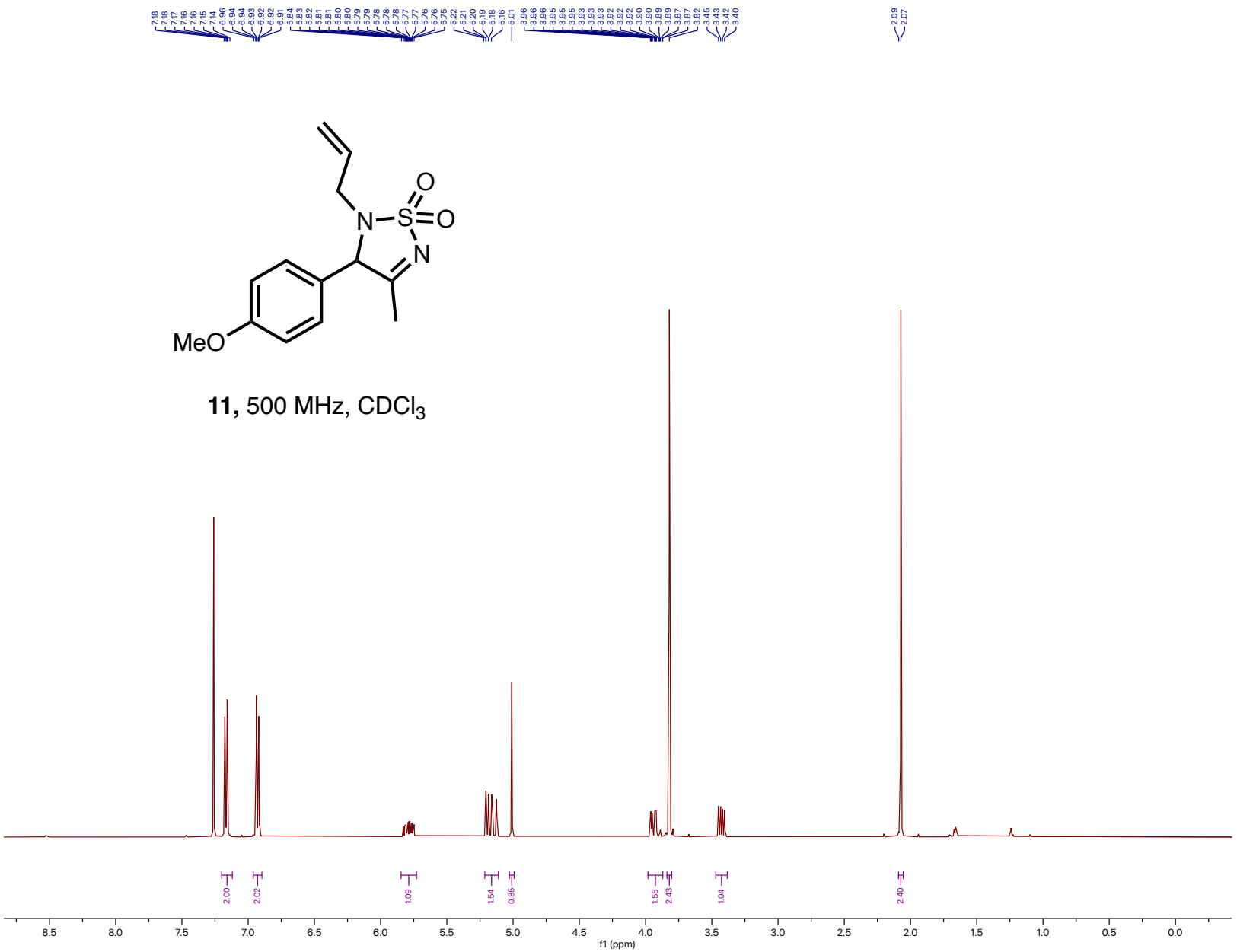




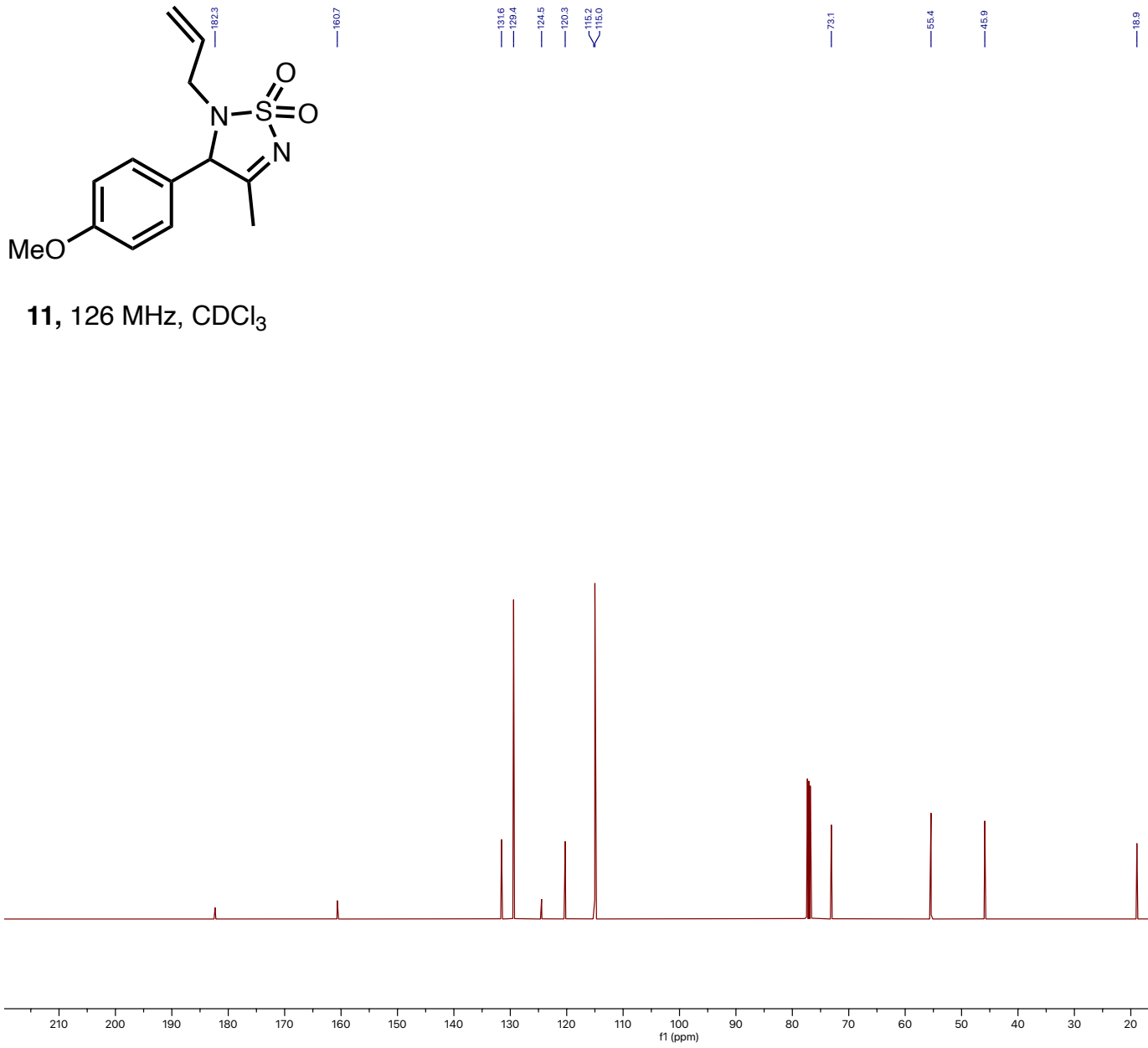
3ab, 400 MHz, $CDCl_3$



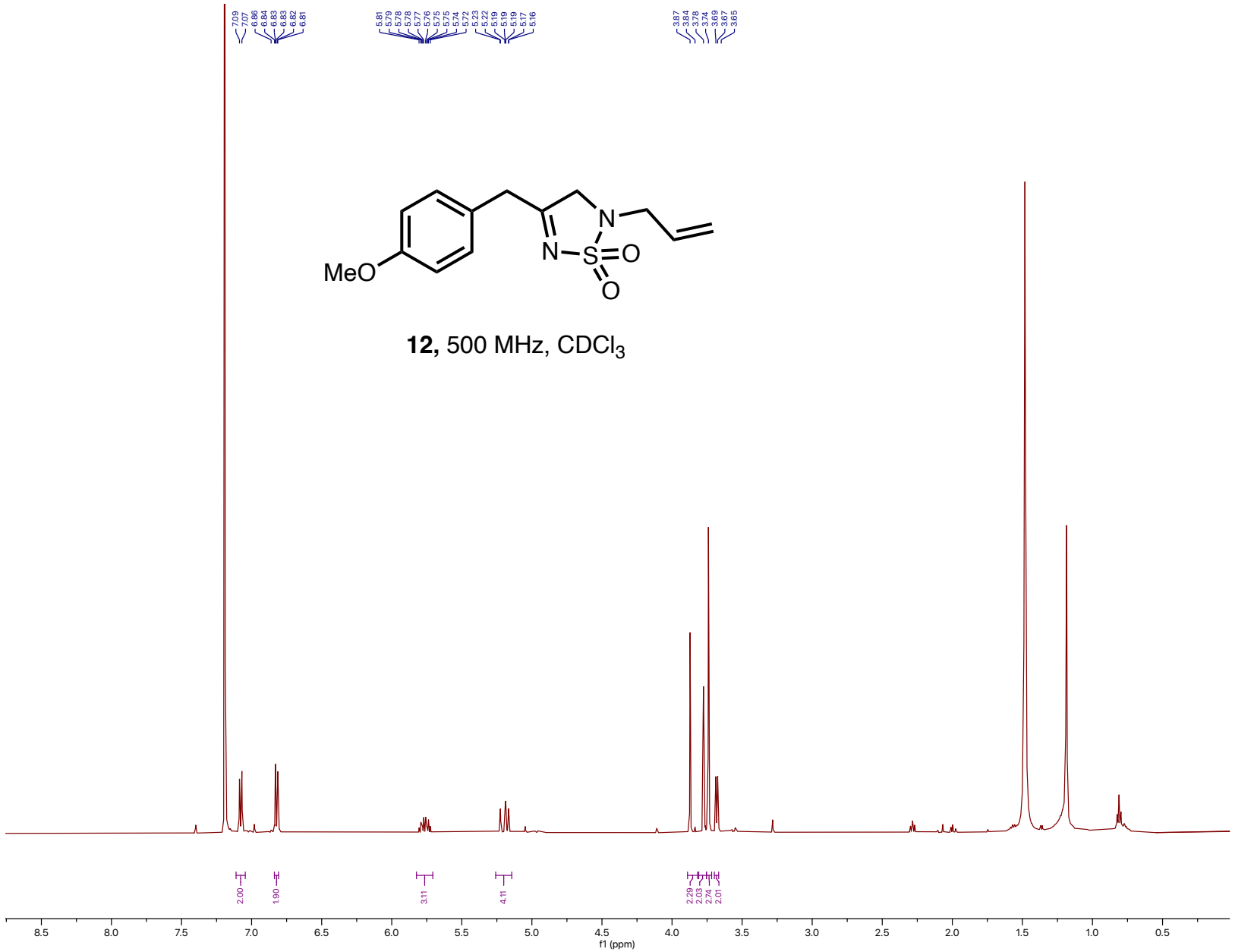
3ab, 101 MHz, $CDCl_3$



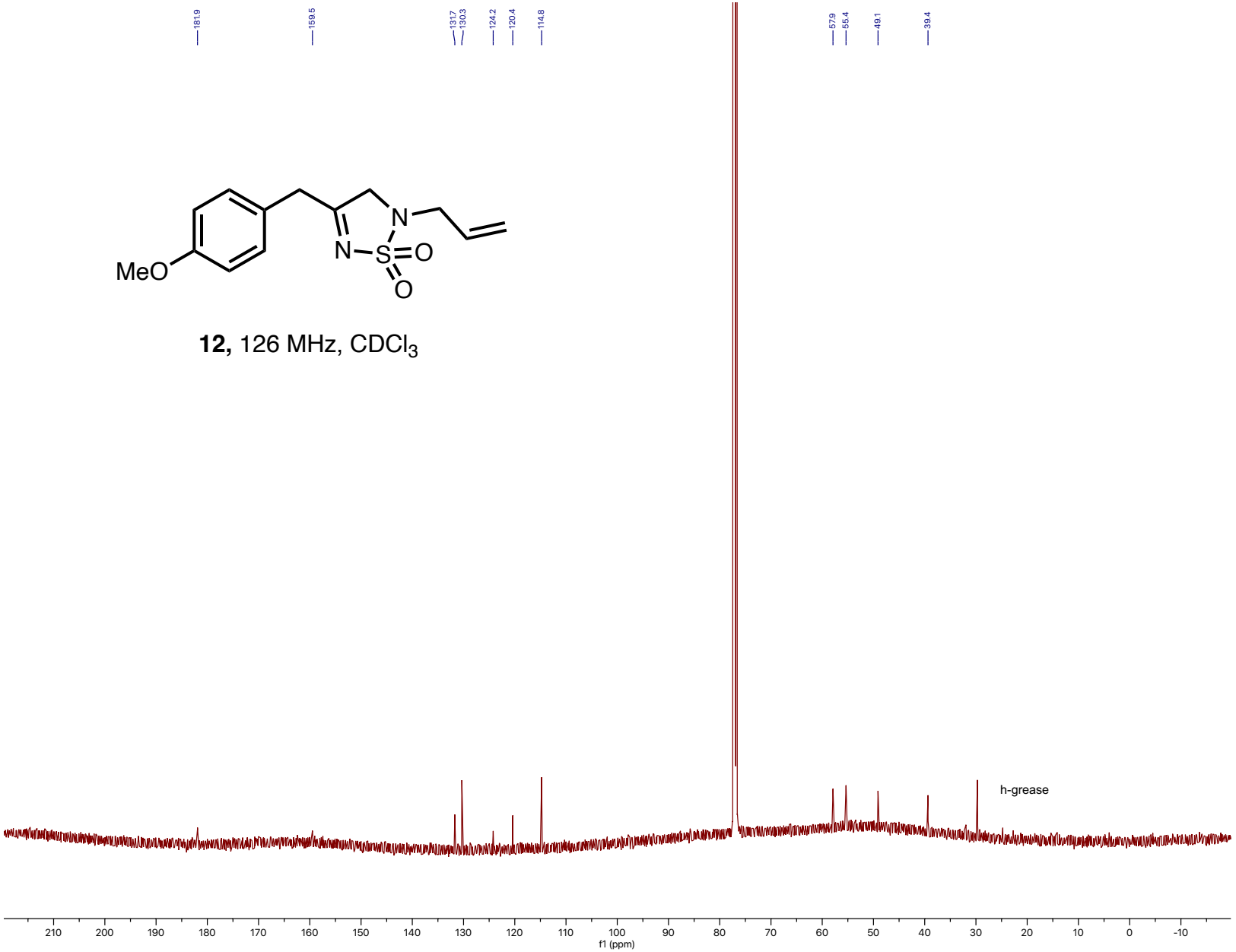
11, 500 MHz, $CDCl_3$



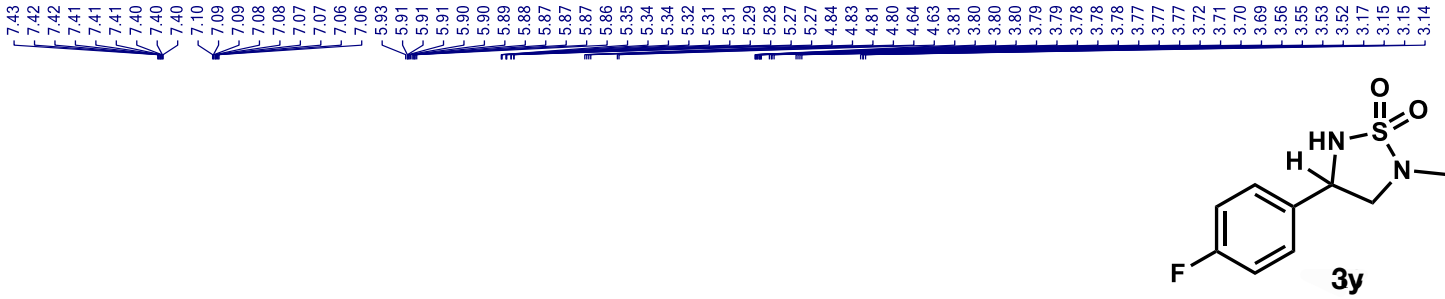
11, 126 MHz, $CDCl_3$



12, 500 MHz, $CDCl_3$

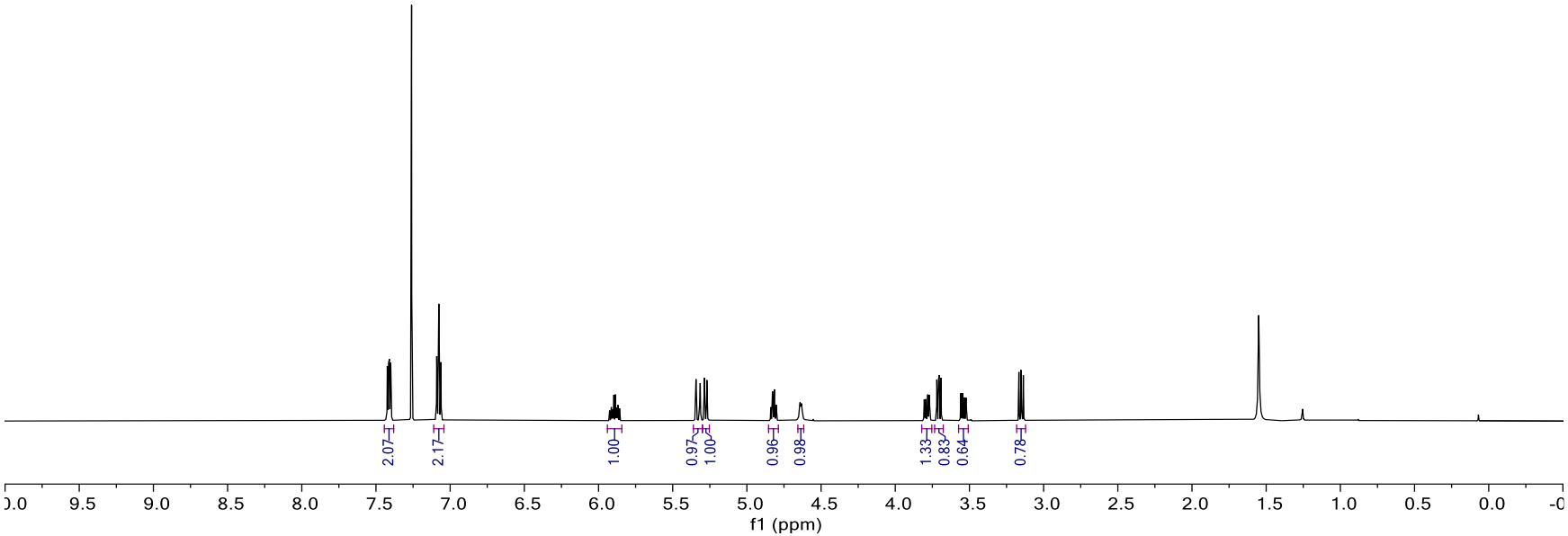


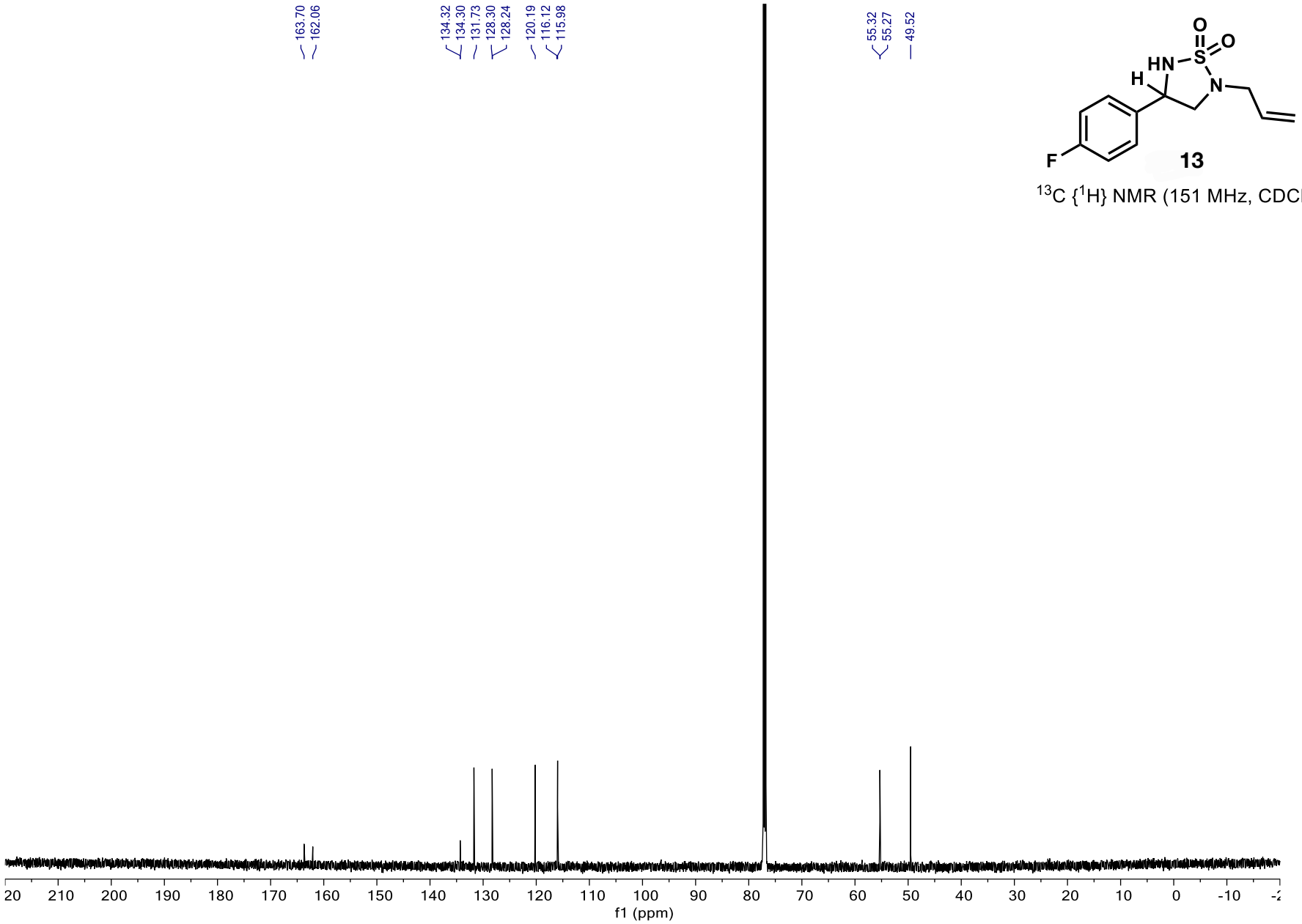
12, 126 MHz, $CDCl_3$



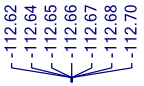
3y

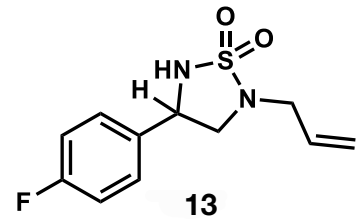
^{1}H NMR (600 MHz, $CDCl_3$)





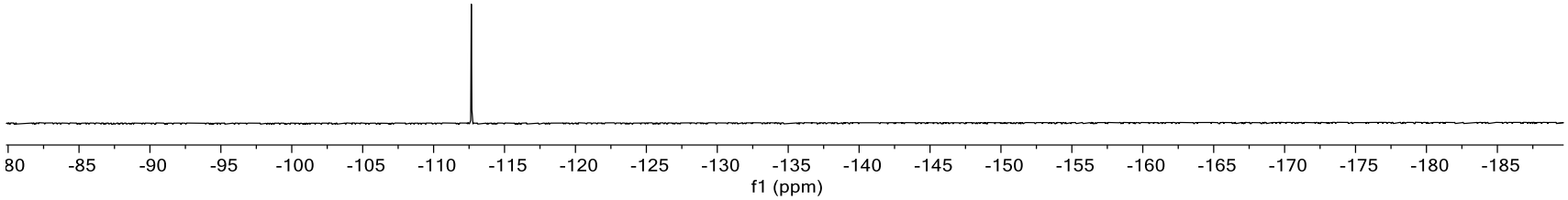
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$)

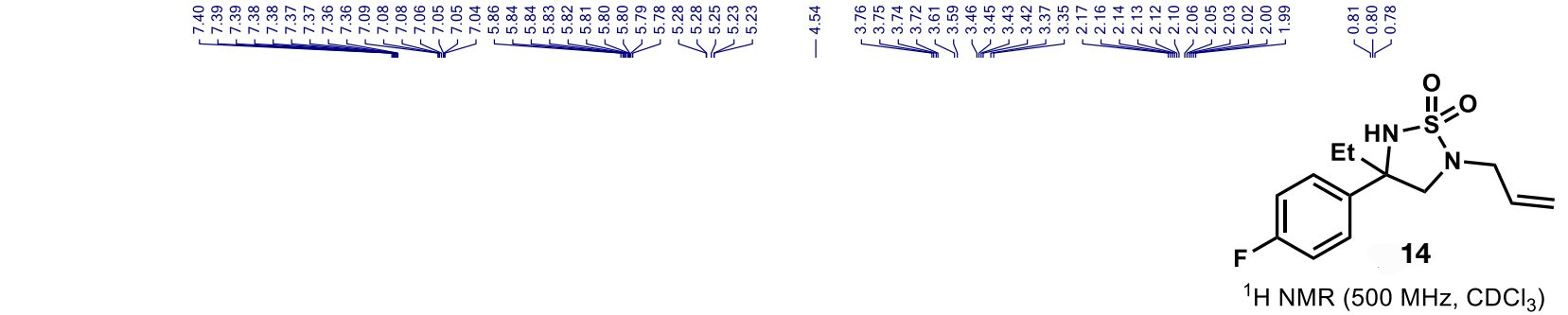




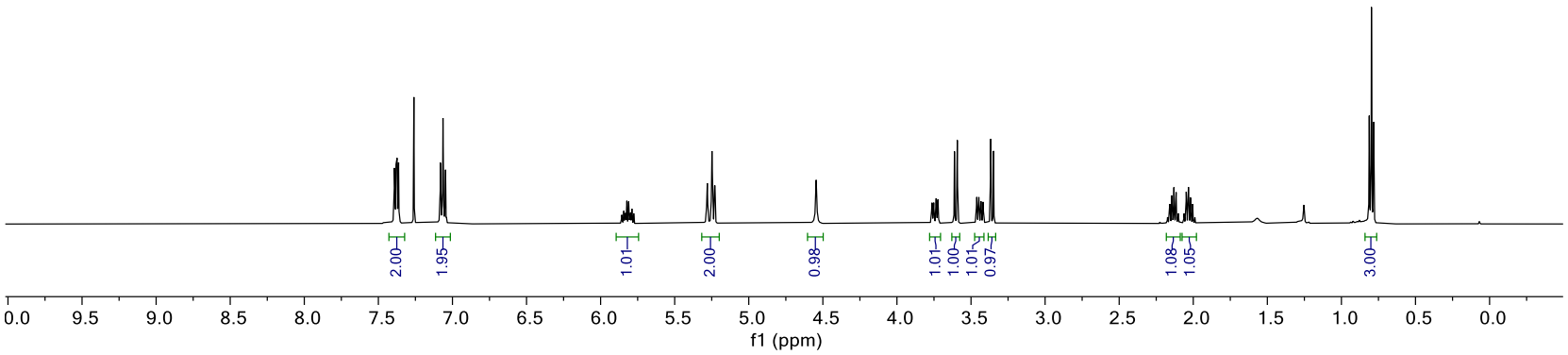
13

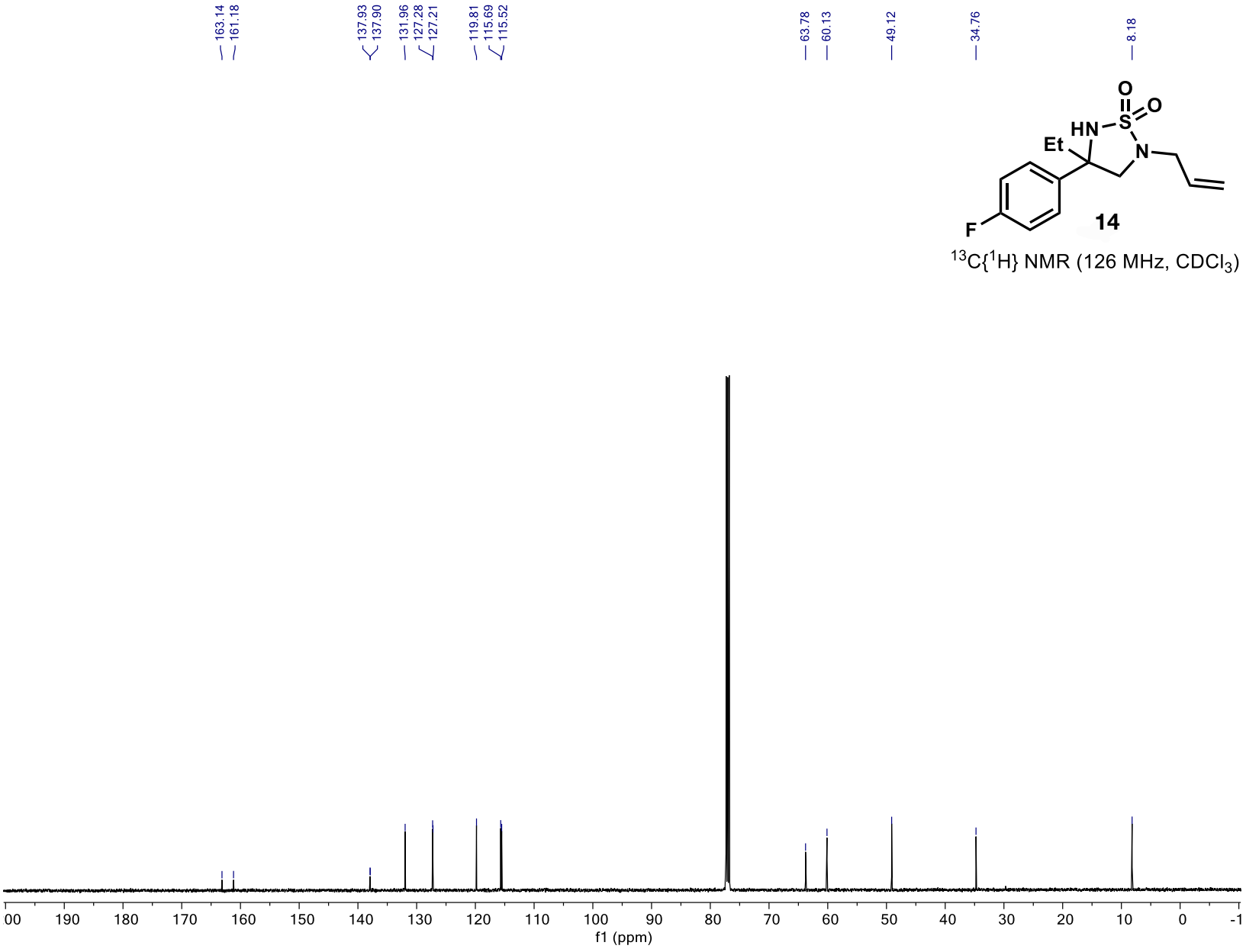
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$)



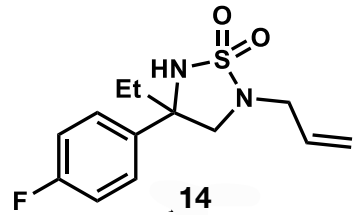


^{1}H NMR (500 MHz, $CDCl_3$)



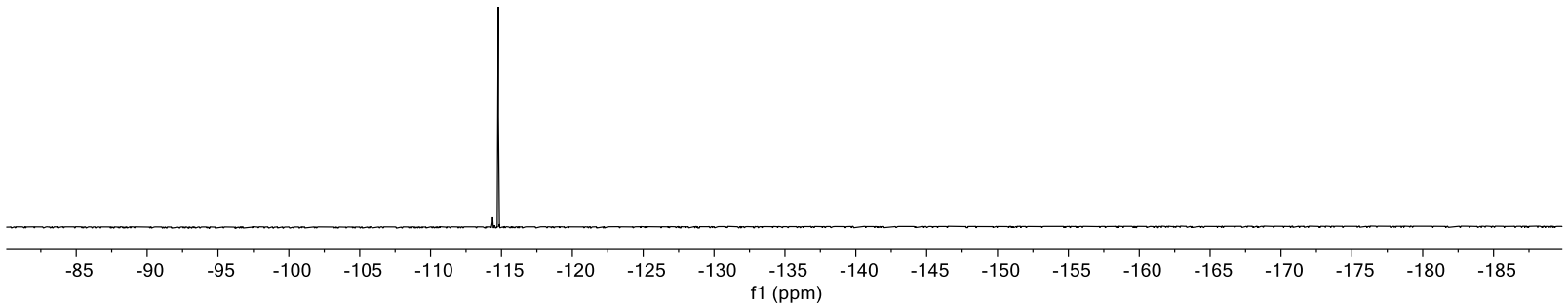

163.14
161.18
137.93
137.90
131.96
127.28
127.21
119.81
115.69
115.52
63.78
60.13
49.12
34.76
8.18
O
O
HN
S
Et
N
F
14
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)
f1 (ppm)

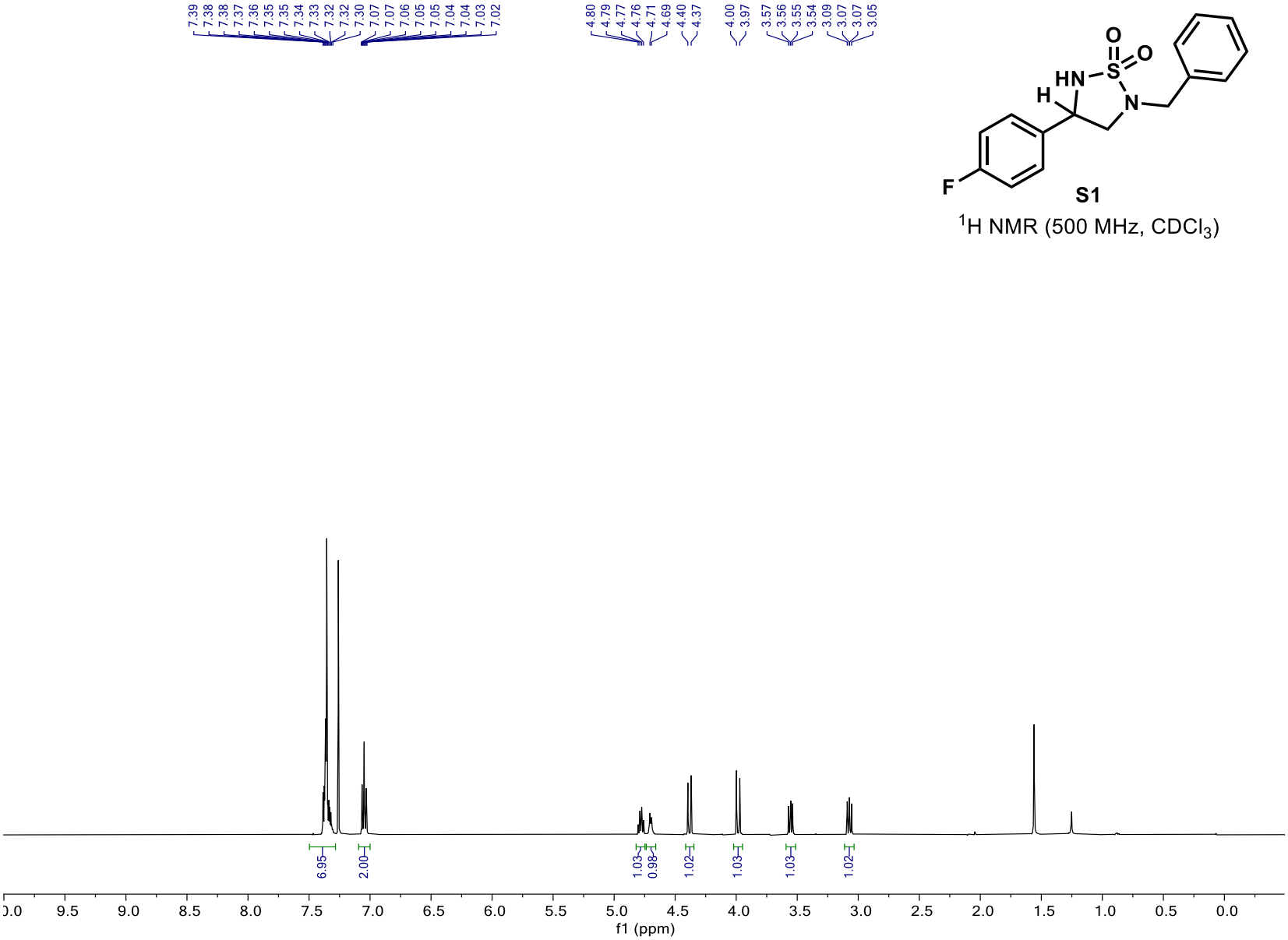
-114.74
-114.75
-114.76
-114.76
-114.77
-114.78
-114.79
-114.80
-114.81



14

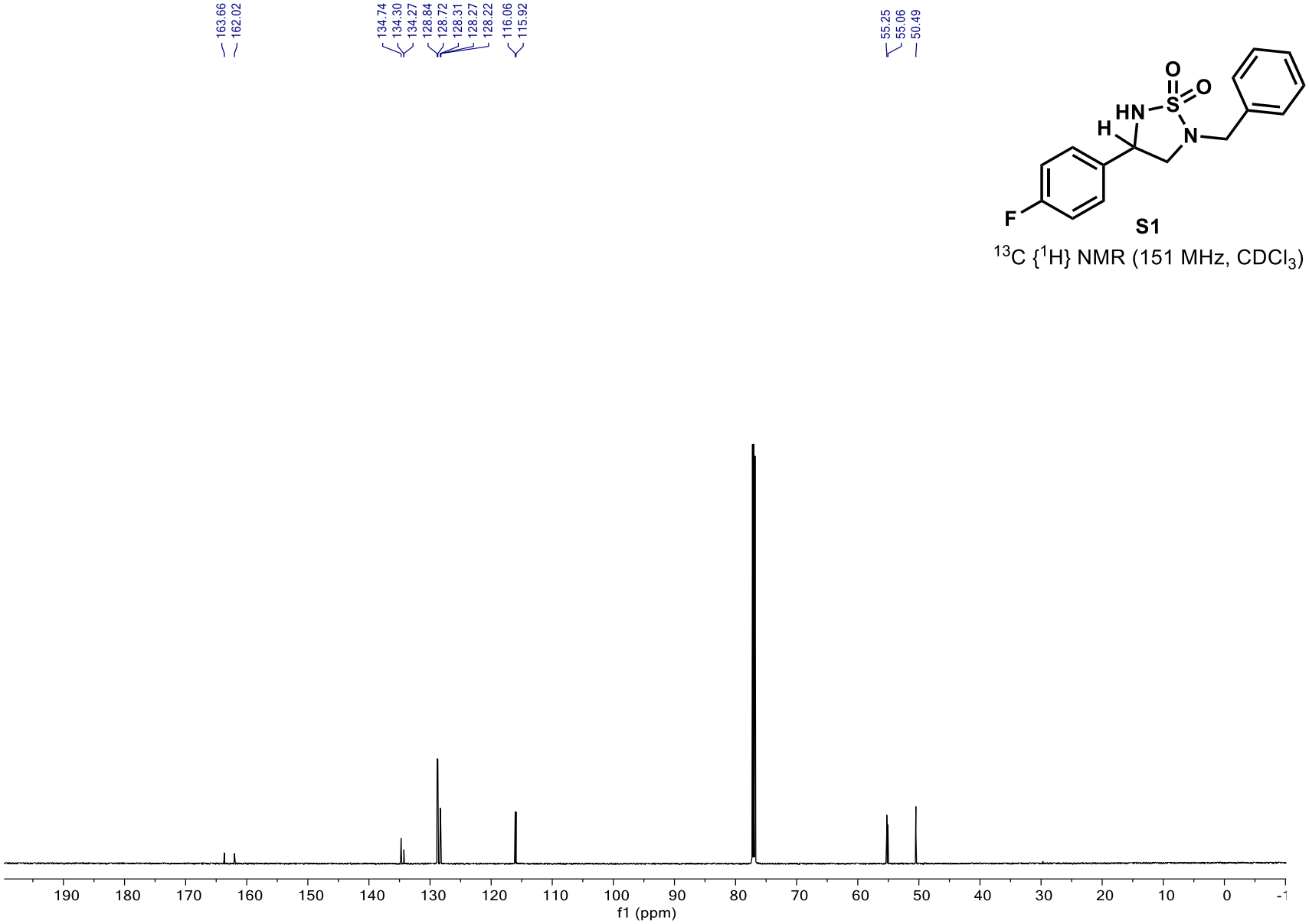
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)





S1

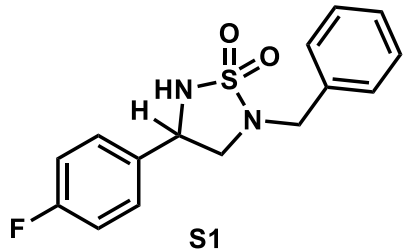
^{1}H NMR (500 MHz, $CDCl_3$)



S1

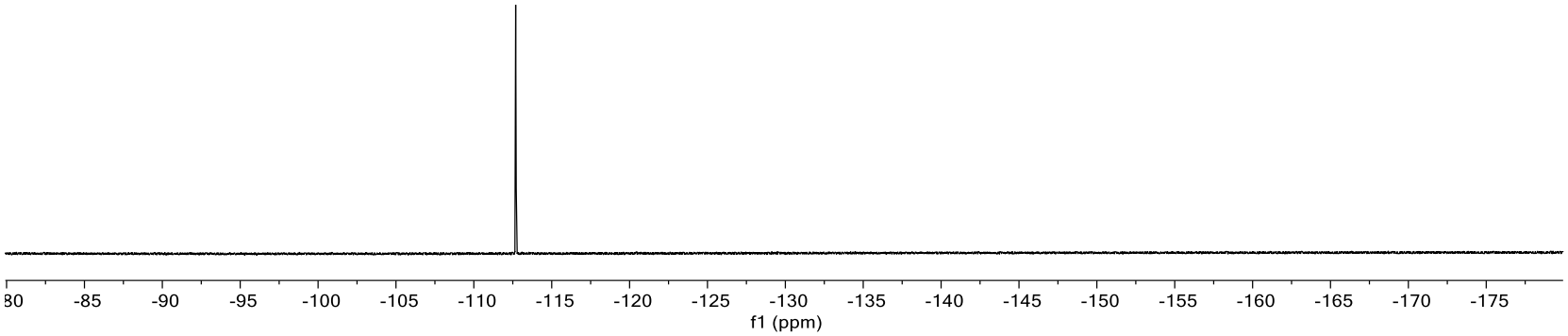
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$)

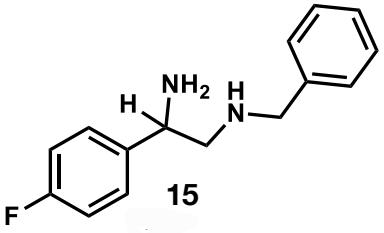
-112.65
-112.66
-112.67
-112.68
-112.69
-112.69
-112.70
-112.71
-112.72



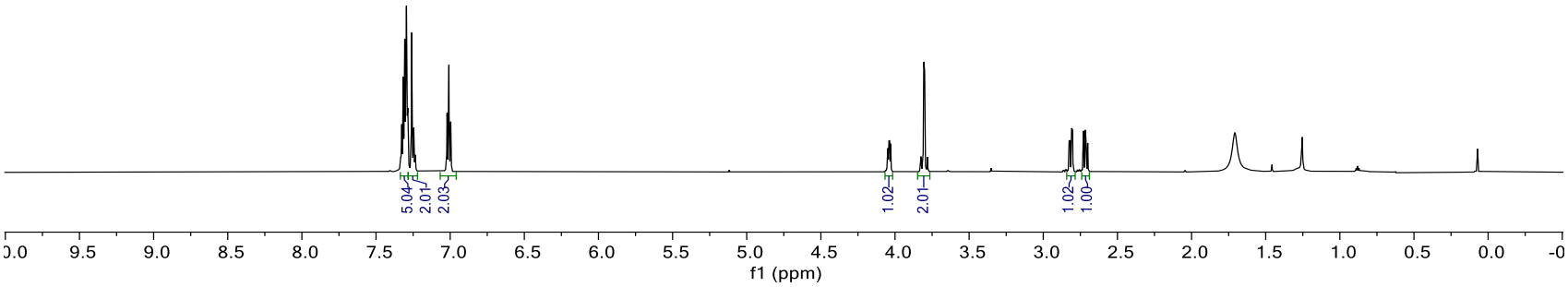
S1

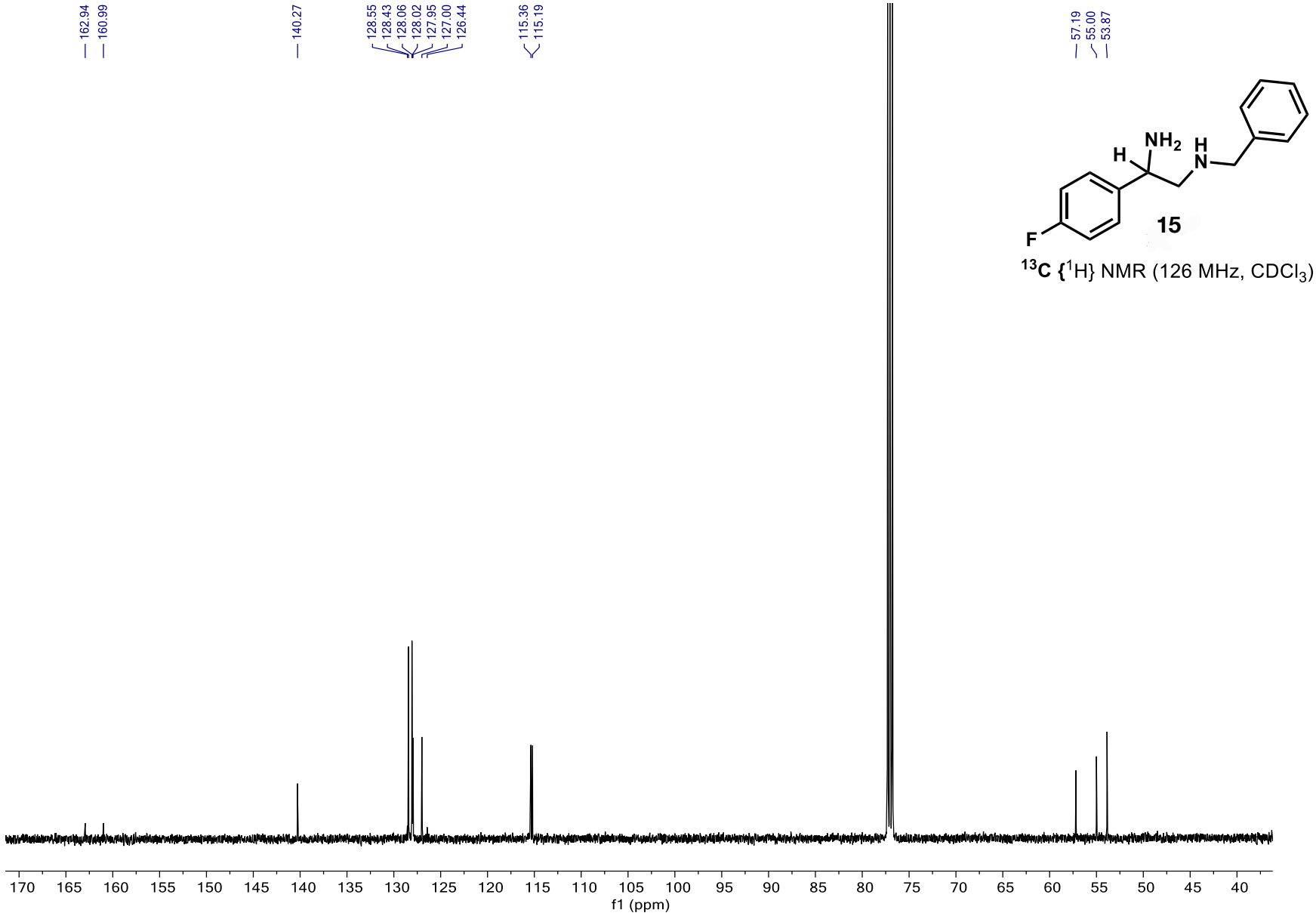
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$)

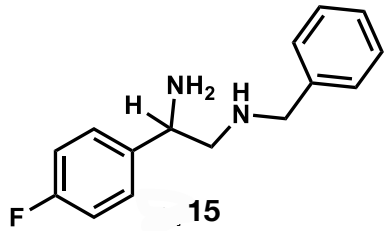




^{1}H NMR (700 MHz, $CDCl_3$)

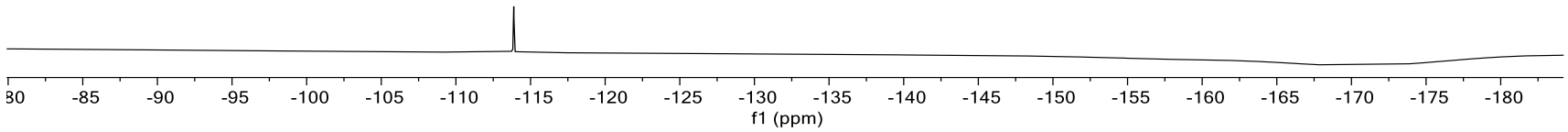


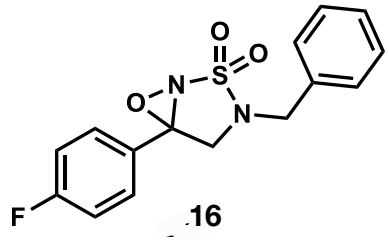

162.94
160.99
140.27
128.55
128.43
128.06
128.02
127.95
127.00
126.44
115.36
115.19
57.19
55.00
53.87
NH2
H
H
N
F
15
13C {1H} NMR (126 MHz, CDCl3)
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)



15

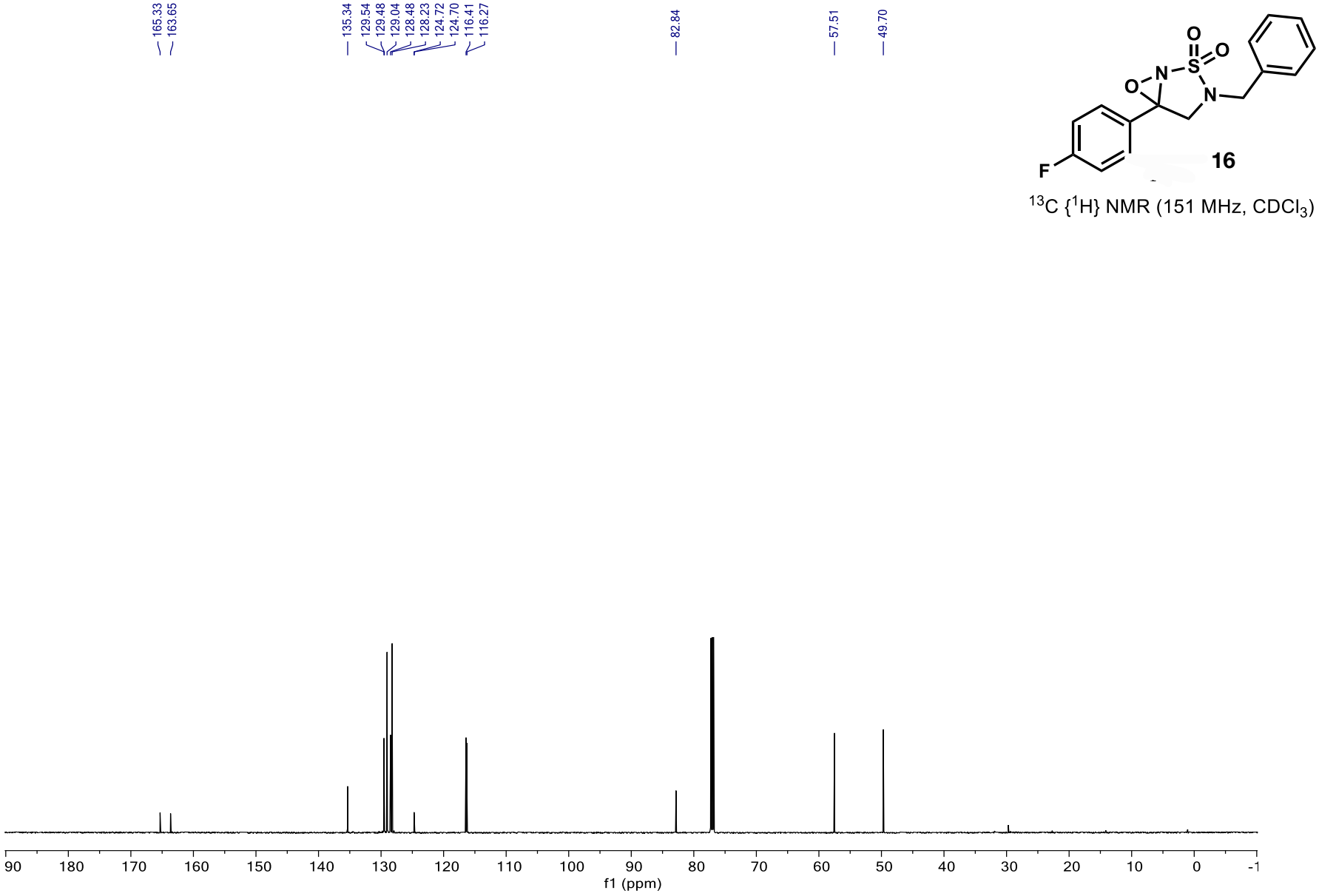
^{19}F {^{1}H} NMR (565 MHz, $CDCl_3$)





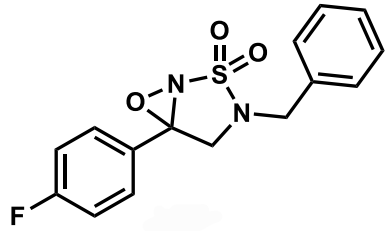
16

^{1}H NMR (600 MHz, $CDCl_3$)

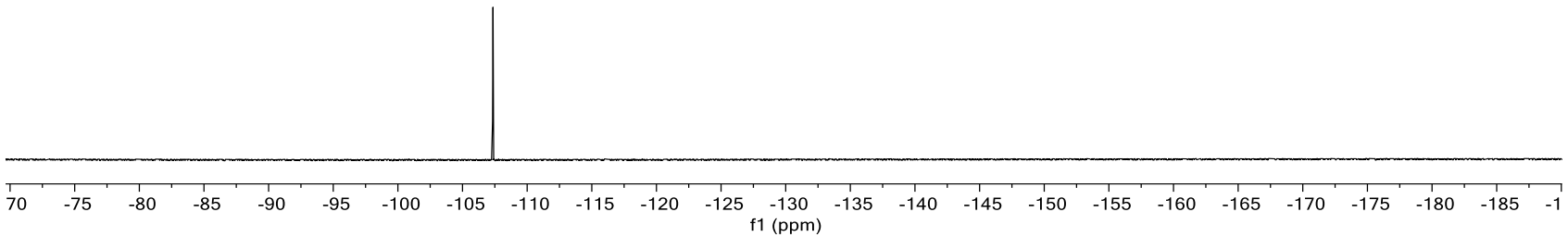


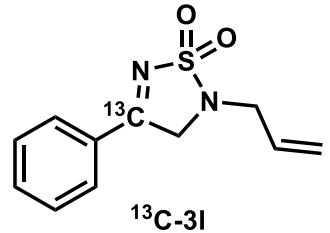
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$)

-107.32
-107.34
-107.35
-107.35
-107.36
-107.37
-107.37
-107.38
-107.40



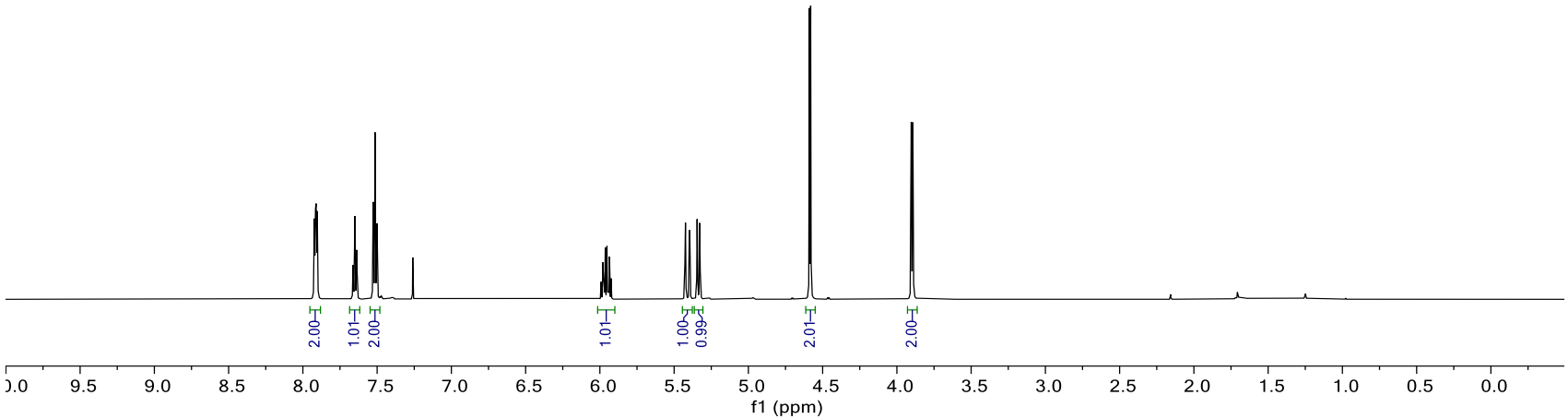
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$)

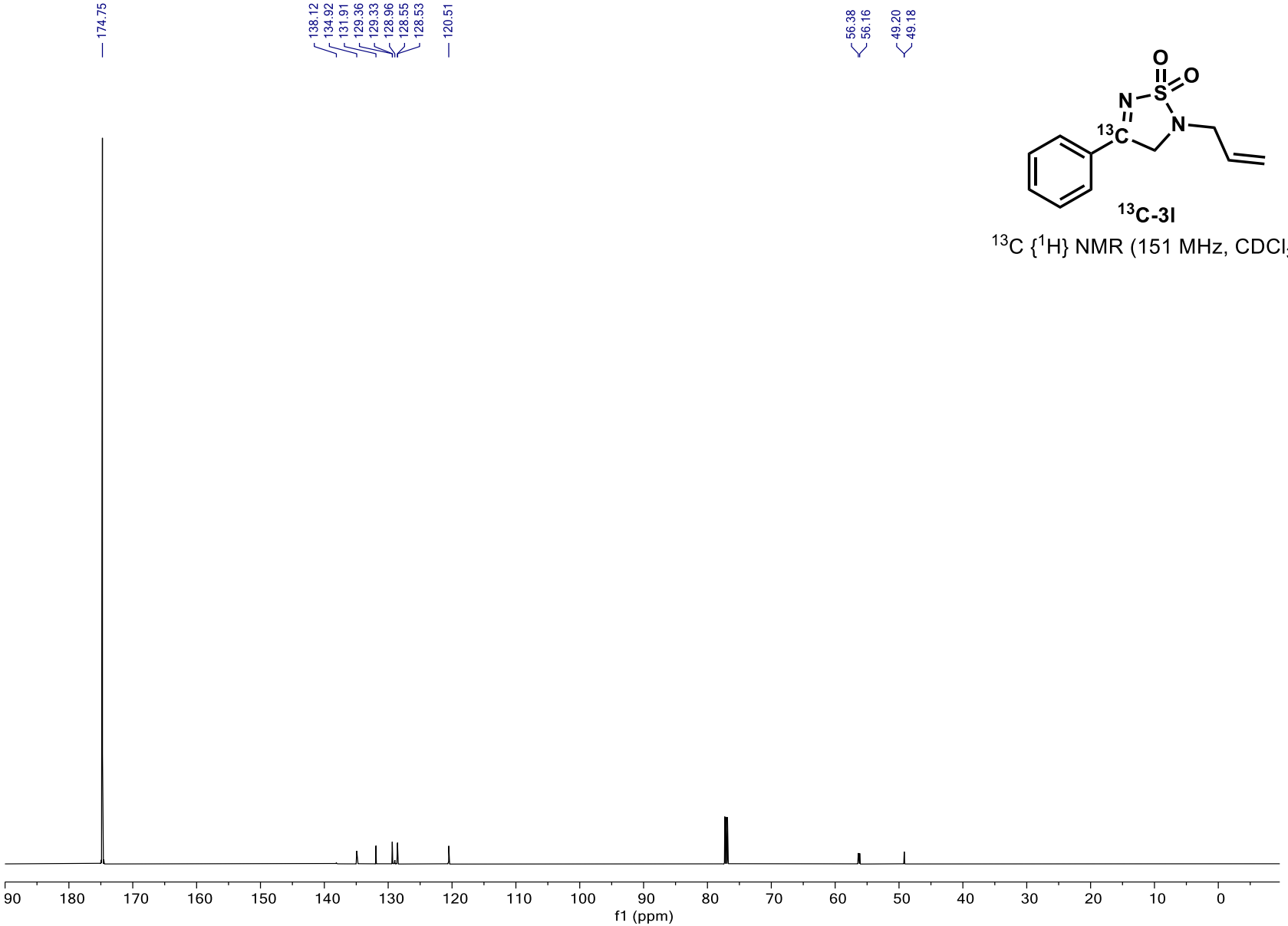




^{13}C-3l

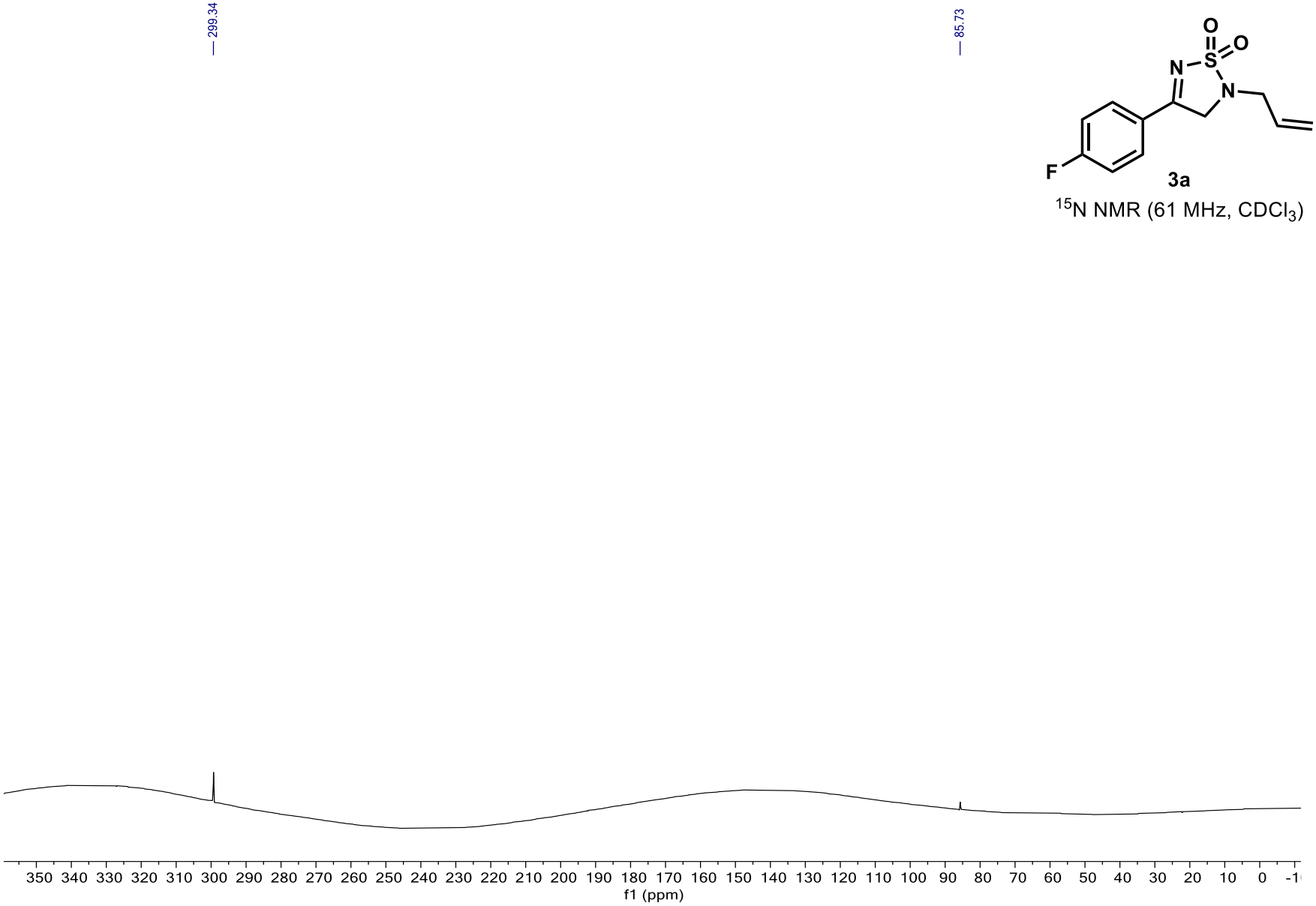
^{1}H NMR (600 MHz, $CDCl_3$)





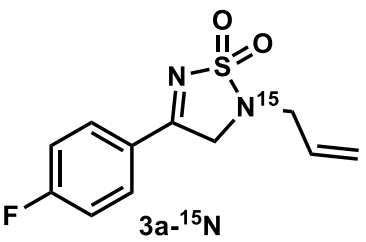
^{13}C-3l

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$)



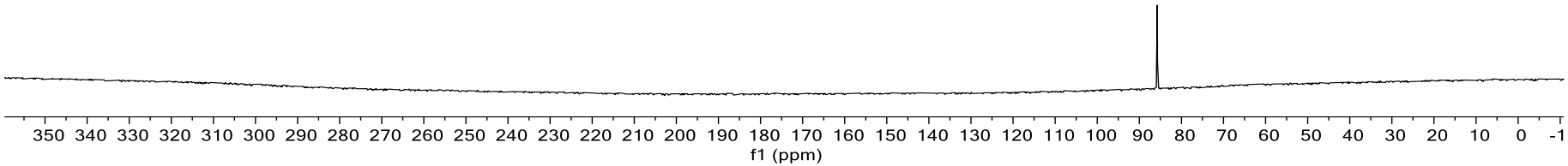
3a

^{15}N NMR (61 MHz, $CDCl_3$)

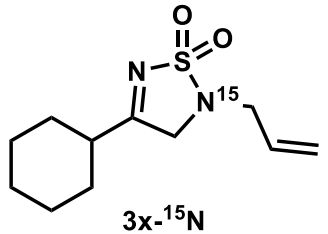


3a-^{15}N

^{15}N NMR (61 MHz, $CDCl_3$)

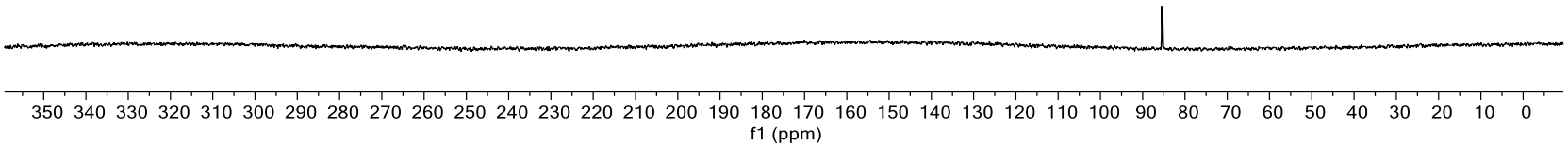


— 85.52

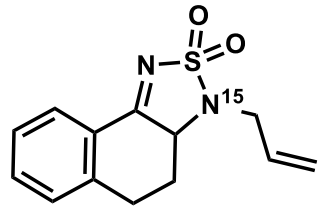


3x-^{15}N

^{15}N NMR (61 MHz, $CDCl_3$)

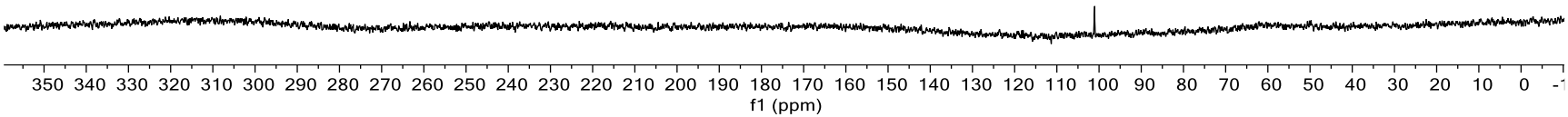


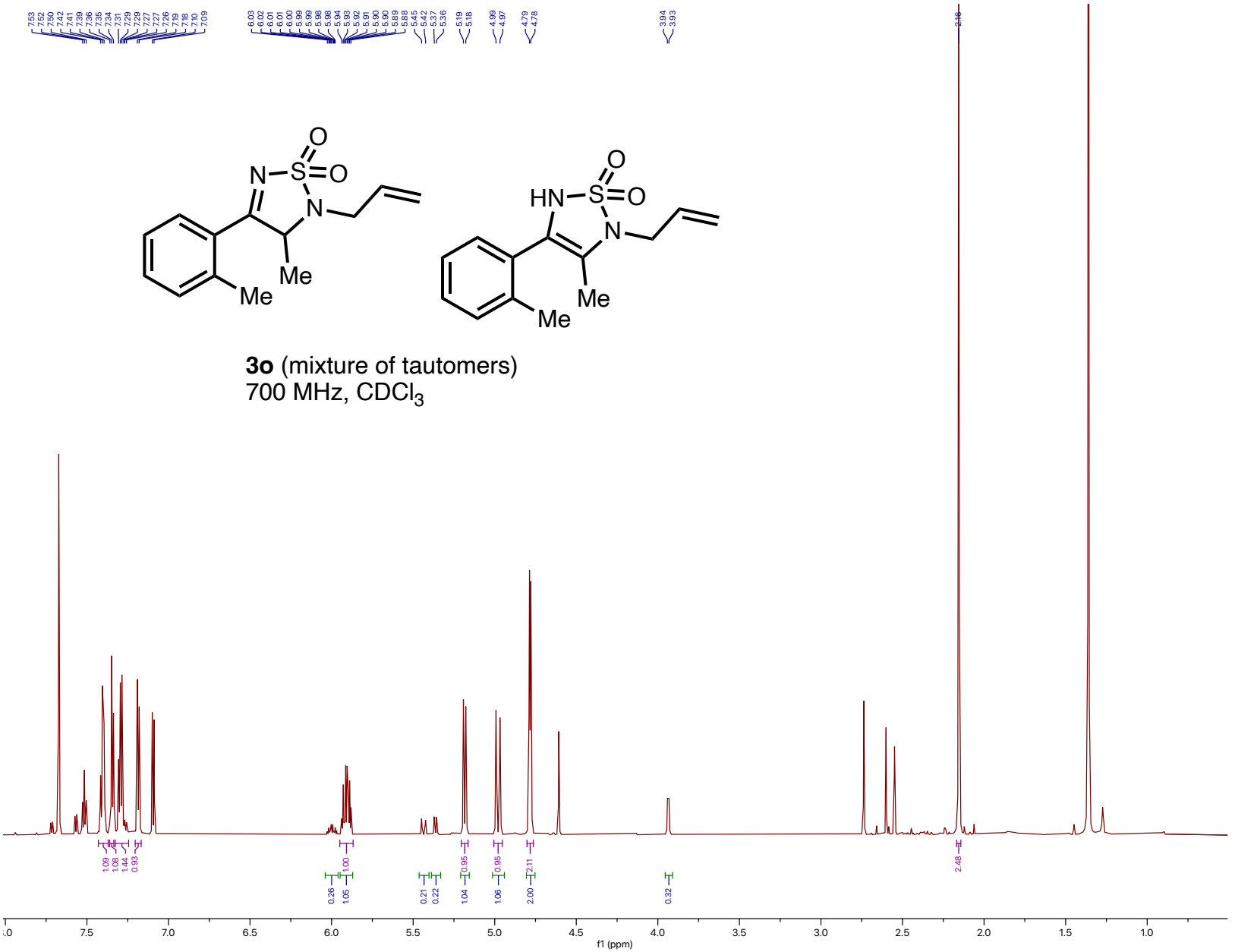
101.04



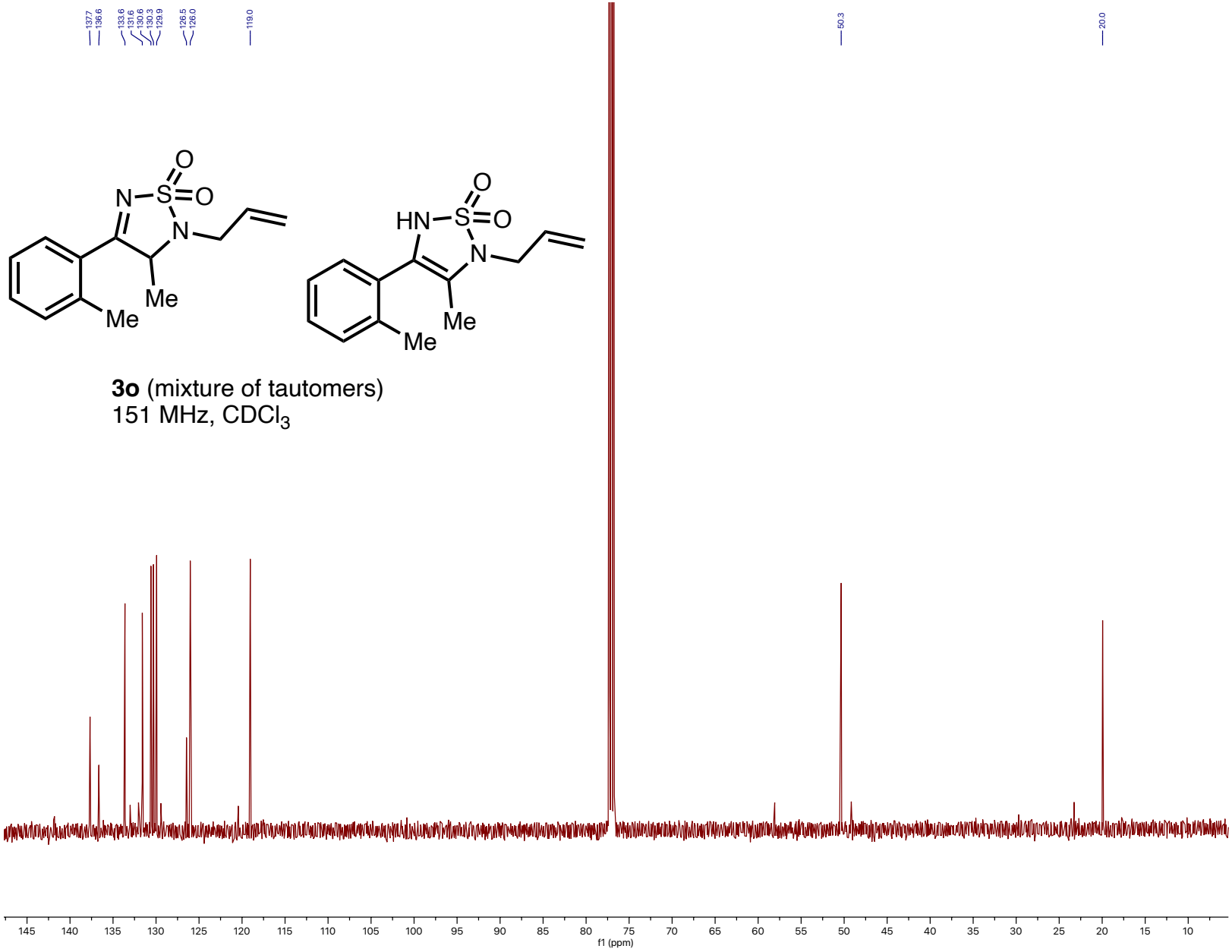
3w-^{15}N

^{15}N NMR (61 MHz, $CDCl_3$)





3o (mixture of tautomers)
700 MHz, $CDCl_3$



3o (mixture of tautomers)
151 MHz, $CDCl_3$